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(71) Applicant (for all consenting  
states except US) BASF AG, Ludwigshafen

(72) Inventor, and

(75) Inventor/applicant (only for US) Peter Schuhmacher, Hans Kricheldorf, Thorsen Krawinkel

(74) Representative: Werner Kinzebach

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(54) Title: CHOLESTERIC OLIGOMERS WITH CROSS-LINKED END GROUPS

(57) ABSTRACT:

The invention relates to cholesteric oligomers of formula (I)  $[(Z_0^1-Y^1-)(A-Y^2-)_q(B-Y^3-)_p]Z^2$ , wherein n represents a value from 0 to 1 in the agent. q represents a value from 0.1 to 2 in the agent. p represents a value from 1 to 20 in the agent. A represents a chiral group, B represents a mesogene group. Y<sup>1</sup>, Y<sup>2</sup> and Y<sup>3</sup>, independent of one another, represent a group of formula -CO-O-, -O-CO- or -O-CO-O-, whereby the q-units (A-Y<sup>2</sup>-) and the p-units (B-Y<sup>3</sup>-) exist in any sequence, the q-groups A are the same or different and the p-groups B are also the same or different. In addition, Z<sup>1</sup> and Z<sup>2</sup>, independent of one another, represent a group of formula W-Q-, wherein Q represents a chemical bonding or one or multiple substituted alkylene-spacers or arylene-spacers, and W represents a cross-linked heterocyclic group. The invention also relates to a method for producing and utilizing said cholesteric oligomers.



## Description

The invention concerns cholesteric oligomers with cross linkable end groups, a process for their production and their application.

Upon the heating of shape-anisotropic substances liquid-crystalline phases so called mesophases occur. The individual phases differ in the steric arrangement of the molecule heavy points, on the one hand, and in the molecule arrangement in terms of the longitudinal axis, on the other (G. W. Gray, P. A. Winsor, Liquid Crystals and Plastic Crystals, Ellis Horwood Limited, Chichester 1974). The nematic liquid crystalline phase is characterized by parallel orientation of the longitudinal axis of the molecules (one dimensional state of ordering). Under the assumption that the molecules building the nematic phase are chiral, a so called chiral nematic (cholesteric) phase arises in which the longitudinal axis of the molecules form a helical superstructure perpendicular to it (H. Baessler, Festkorperprobleme XI, 1971). The chiral part of the molecule can be present both in the liquid crystalline molecule itself and also may be added as a doping substance to the nematic phase, in which case the chiral nematic phase is induced. This phenomenon was first studied on cholesterol derivatives (e.g. H. Baessler, M. M. Labes, J. Chem. Phys. 52, 63 (1970)).

The chiral nematic phase has special optical properties: a high optic rotation and a pronounced circular dichroism which arises due to selective reflection of circularly polarized light inside the chiral nematic layer. If the pitch height of the helical superstructure corresponds to the wavelength of visible light, the formation of a so called Grandjean texture occurs. The colors which appear different depending on the viewing angle depend on the pitch height of the helical superstructure which in turn depends on the twisting power of the chiral component. In this case in particular by changing the concentration of a chiral doping substance the pitch height and with it the wavelength range of the selectively reflected light of a chiral nematic layer can be

varied. Such chiral nematic systems offer interesting possibilities for practical application. Thus by incorporating chiral molecule parts in mesogenic acrylic acid esters and orientation in the chiral nematic phase, e.g., after photocrosslinking, a stable, colored network can be produced whose concentration of chiral components, however, then can no longer be changed (G. Galli, M. Laus, A. Angelon, Makromol. Chemie 187, 2289 (1986)). By mixing uncrosslinkable chiral compounds into nematic acrylic acid structures, by photocrosslinking a colored polymer can be produced which still contains high contents of soluble components (I. Heyndricks, D. J. Broer, Mol. Cryst. Liq. Cryst., 203, 113 (1991)). Furthermore by statistical hydrosilylation of mixtures of cholesterol derivatives and acrylate-containing mesogens with defined cyclic siloxanes and subsequent photopolymerization a chiral nematic network can be obtained in which the chiral component may have a content of up to 50% of the material used; these polymers, however, still contain distinct quantities of soluble components (F.H. Kreuzer, R. Mauerer, Ch. Muller-Rees, J. Stohrer, Report No. 7, 22, Working meeting on liquid crystals, Freiburg, 1993).

In DE-A-35-35 547 a process is described in which a mixture of cholesterol-containing monoacrylates can be fabricated via photocrosslinking into chiral nematic layers. To be sure, the total content of chiral component in the mixture amounts to circa 94%. As a pure side chain polymer such a material is mechanically not very stable, but an increase in the stability can be achieved by highly crosslinking diluting agents.

Also numerous chiral nematic polyesters in which the mesogen structures are incorporated into the main chain are well known, e.g. from S. Vilasagar, A. Blumstein, Mol. Cryst. Liq. Cryst. (1980), 56 (8), 263-9; A. Blumstein, S. Vilasagar, S. Ponratham, S. B. Clough, R.B. Blumstein, G. Maret, J. Polym. Sci., Polym. Phys. Ed. (1982), 20 (5), 877-92; E. Chiellini, G. Galli, C. Malanga, N. Spassky, Polym. Bull.(1983), 9 (6-7), 336-43; H. J. Park, J. I. Jin, R. W. Leng, polymer (1985), 26 (9), 1301-6; J. I. Jin, E. J. Choi, K. Y. Lee, Polym. J. (1986), 18 (1),

99.101; J.I. Jin, S. C. Lee, S. D. Chi, J. H. Chang; Pollimo (1986) 10 (4), 382-8; J. I. Jin, E. J. Choi, B. W. Jo, Pollimo (1986), 10 (6), 635-40; J. M. G. Cowie, H.H. Wu, *Markromol. Chem.* (1988), 189 (7), 1511-16; V. V. Zuev, I. G. Denisov, S. S. Skorokhodov, *Vysokomol. Soedin., Ser. A* (1989, 31 (5), 1056-61; A. S. Angeloni, D Caretti, C. Carlini, E. Chiellini, G. Galli, A. Altomare, R. Solaro, M. Laus, *Liq. Cryst.* (1986), 4 (5), 513-27; K. Fujishiro, R. W. Lenz, *Macromolecules* (1992), 25 (1), 88-95; K. Fujishiro, R. W. Lenz, *Macromolecules* (1992), 25 (1), 81-7; V. V. Zuev, I. G. Denisov, S. S. Skorokhodov, *Vysokomol. Soedin., Ser. B* (1992), 34 (3), 47-54); V. V. Zuev, I. G. Denisov, S. S. Skorokhodov *Vysokomol. Soedin., B* (1989), 31 (2), 130-2.

These polyesters as a rule display narrow ranges of existence of the chiral nematic phase and contain predominantly open-chained chiral components which possess a low twisting capacity so that relatively large contents of these components are necessary in order to achieve a color impression. As a result the choice of the remaining polyester constituents is limited, for example, in terms of their mechanical properties.

DE-A-19 538 700 describes polymers forming cholesteric phases which contain at least one bifunctional chiral molecule building block, at least one bifunctional chiral or racemic molecule building block and at least one bifunctional molecule building block which may be arbitrarily chiral or achiral and which differs from the 2 first-mentioned molecule building blocks. The polymers described are suitable as granulate for molding compounds for further processing, e.g., by injection molding processes. They can also be fabricated into pigments for iridescent enamels.

EP-A 682 092 described enamels based on chiral nematic cinnamic acid group-containing polymers which can be crosslinked by UV irradiation but not thermally. As examples polyesters produced by polycondensation of dicarboxylic acids and diols are mentioned.

From DE-A 44 41 651 a process is known for surface treatment or coating of substrates with a coating agent which contains at least one polymerizable low-molecular liquid crystalline compound. In addition the use of especially photochemically polymerizable low-molecular liquid-crystalline compounds (oligoesters) in printing inks, inks and enamel systems have been described.

WO-A-96/02 597 describes a process for coating or imprinting substrates with a coating or printing agent which contains a chiral or achiral liquid crystalline monomer and a nonliquid crystalline chiral compound. The liquid crystalline monomers are preferably photochemically polymerizable bis-acrylates.

WO-A-95/29 962 describes aqueous coating agents for production of coatings whose color impression depends on the viewing angle and which contain flakelike pigments of oriented, three dimensionally crosslinked substances of liquid crystalline structure with a chiral phase. As especially preferred substances three-dimensionally crosslinkable polyorganosiloxanes are described.

From WO-A-95/29 961 coating agents with viewing angle-dependent color impression and their use in base enamels for multilayered enamel coatings are known. The agents contain flakelike pigments with viewing-angle-dependent color which consist of oriented, three-dimensionally crosslinked substances of liquid-crystalline structure with a chiral phase. 3-dimensionally cross linkable polyorganall salaxanes are described as preferred substances.

DE-A-44 18 076 describes an effect enamel or an effect enamel coating involving the use of liquid-crystalline interference pigments. The interference pigments consist of esterified cellulose ethers, especially acylated hydroxypropyl cellulose.

From EP-A-7 24 005 a pigment is known with viewing-angle-dependent color impressions, its production and use in an enamel. The pigment is obtained by three-dimensional

crosslinking of oriented substances of liquid-crystalline structure with a chiral phase. Preferred substances are three-dimensionally crosslinkable polyorganosiloxanes. In order to make the pigment hold color at elevated temperatures it is proposed that the crosslinking be carried out in the presence of at least one other color-neutral compound which contains at least 2 crosslinkable double bonds. As the preferred color-neutral compounds acrylates, polyurethanes, epoxides, siloxanes, polyesters and alkyd resins are named.

EP-A-686 674 and the priority application on which they are based DE-A-44 16 191 describe interference pigments of molecules fixed in a cholesteric arrangement and their application. The pigments described display a flakelike structure and a thickness of 7  $\mu\text{m}$ . They contain oriented crosslinked substances of liquid-crystalline structure with a chiral phase, preferably polyorganosiloxanes.

EP-A-601 483 and the priority application on which it is based DE-A-42 40 743 describe pigments with a color impression dependent on the viewing angle, their production and application. The pigments described consist of oriented three-dimensionally crosslinked substances of liquid-crystalline structure with a chiral phase, preferably polyorganosiloxanes and possibly other pigments and dyestuffs.

DE-A 19 502 413 describes a pigment with viewing-angle-dependent color which was obtained by three-dimensional crosslinking of oriented substances of liquid-crystalline structure with a chiral phase. In order to make such a pigment maintain its color at elevated temperatures it is proposed that the crosslinking be conducted in the presence of at least one other color-neutral compound containing at least two crosslinkable double bonds.

DE-A-19 704 506 describes liquid crystalline chiral nematic polyesters with flexible chains which include isosorbide, isomannide and/or isoidide units. The polyesters are not

crystalline and form Grandjean textures which can be frozen upon cooling below the glass transition point. They are therefore especially useful as surface coating materials.

From P. M. Hergenrother, Encyclopedia of polymers 1, 61 (1985). Acetylene-terminated prepolymers are known (page 61-86) as well as polymers which contain propargyl groups in the side chains (p. 82f). The compounds described are thermally crosslinkable.

From P. M. Hergenrother et al., Journal of Polymer Science: Part A: Polymer Chemistry, 32, 3061-3067 (1994) phenylacetylenyl-terminated oligo/polyimides are known which are not cholesteric and can be crosslinked at high temperatures without liberation of volatile substances. The crosslinked polymers described are said to be more stable with respect to thermal oxidation than those produced from acetylene-terminated oligomers.

US-A-4-166 168 describes non-cholesteric acetylene-terminated polyimide esters and their thermal crosslinking to produce insoluble nonmelting polymers without forming secondary products.

Wang, C.-S. and Hwang, H.-J. in the Journal of Polymer Science, part A: Polymer Chemistry, 34, 1493-1500 (1996) describe bismaleimide-containing non-cholesteric naphthalene units and their thermal crosslinking. The crosslinking products are thermally stable, display a high resistance to chemicals and absorb only a little moisture.

From Hoyt A. E. and Benicewicz, B. C., Journal of Polymer Science: Part A: Polymer Chemistry, 28, 3403-3415 and 3417-3427 (1990) non-cholesteric liquid crystalline polymers are known which can be obtained by polymerization of monomers terminated with maleimide, norbornene-dicarboxylic acid imide and methylnorbornenedicarboxylic acid imide groups. The malaimide-terminated monomers crosslink more rapidly than the methylnorbornene dicarboxylic acid imide-terminated monomers.

Hao, J. et al. describe in Polymer 37, 16, 3721-3727 (1996) the synthesis of maleimide-terminated polysiloxanes by reaction of N-(4-hydroxyphenyl) maleimide with dichlorodimethylsilane and subsequent reaction with hydroxyl-terminated polysiloxane. The incorporation of the maleimide-terminated polysiloxanes into a matrix of 4,4'-bis-maleimidodiphenylmethane (BMI) in a quantity of about 20 wt.% leads to a considerable mechanical strengthening of the matrix.

From Lin, K.-F. et al., Polymer 37.21, 4729-4737 (1996) the reaction of different noncholesteric bis-maleimides with allylamines is known. The crosslinking products have outstanding mechanical and thermal properties.

Meador, M. A. B. et al. describe in High Perform. Polym. 8, 363-379 (1996) the effects of cyclic heating and cooling of samples of noncholesteric norbornenyl-terminated polyimide resins (PMR-15) on its weight, microhardness and crack formation.

From Barton J. M. et al., Polymer, 33, 17, 3664-3669 (1992) non-cholesteric aryl-bis maleimides and bis citraconimides are known. In particular the thermal polymerization kinetiks of these compounds and the effects of the purity of the monomer on the characteristic of the thermal polymerization are studied.

Habas, J. P. et al. describe in High Perform. Polym., 8, 407-426 (1996) a new non-cholesteric high-tempersture resin (IP960) as an alternative to the above-mentioned PMR-15. The IP960 prepolymers are also norbornenedicarboxylic acid imide-terminated, but differ from PMR-15 prepolymers by the substitution of a carbonyl function for a C-OH group. As opposed to PMR-15 IP960 is said to be capable of storage in the form of dry powder.

US-A-5,475,133 describes thermally crosslinkable diesters which are terminated by 4-propargyloxybenzoic acid or p-propargyloxphenyloxy radicals. Some of the diesters described

as examples have liquid-crystalline properties which, however, are already lost far below the cross linking temperature. No example of crosslinking in the liquid crystalline phase is stated.

WO-A-97/00600 describes polymerizable liquid crystalline compounds which contain a mesogenic group and are terminated with polymerizable radicals. By polymerization with compounds containing a chiral component cholesteric polymerization products can be synthesised which, for example, can be comminuted into pigments. The compounds and compositions described which contain them are said to be characterized by favorable liquid crystalline phase temperature ranges and can be used in optical indicator devices and in cholesteric liquid crystalline coloring agnets or pigments.

DE-A-19631 658 describes chiral nematic polycarbonates which are produced by different types of polycondensation of diols with phosgene or diphosgene. Photoreactive and/or thermally crosslinking groups may be condensed in the form of the corresponding diol compounds. Cinnamic acid chloride may be added as a chain interruptor.

DE-A 195 04 913 describes pyronematic polyesters with strongly twist-acting chiral diol components, especially dianhydro sugars and broad liquid crystalline phase ranges. The polymers may contain cinnamic acid groups which can be crosslinked via a [2+2]-photo-cycloaddition.

From DE-A-19 717 371 propargyl-terminated, nematic or cholesteric oligo/polyester, oligo/polycarbonates or nematic or cholesteric mixtures which contain them are known. The compounds described are thermally crosslinkable at a temperature of about 180 to 340 C. They are especially useful as surface-coating materials.

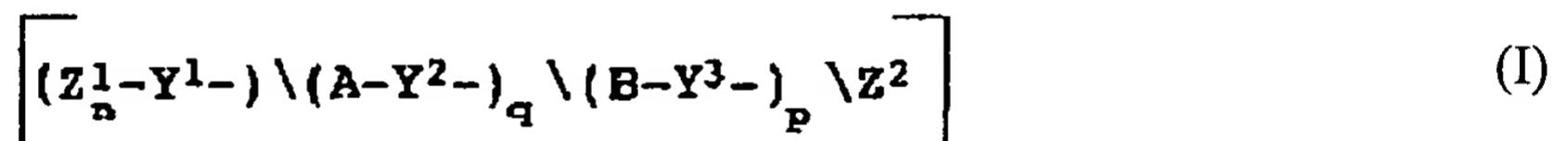
One of the main problems in the preparation of nematic or cholestric oligo/polyesters or oligo/polycarbonates is the fixation of their supermolecular order which conditions the desired optic properties of the oligo/polymers. Various methods for fixation of the supermolecular order

of polymers by crosslinking via bonds have recently been published (H.R. Kricheldorf, N. Probst, M. Gurau, M. Berghahn,; Macromolecules (1995) 28, 6565, J. Stumpe, A. Ziegler, M. Berghahn, H. R. Kricheldorf; Macromolecules (1995) 28, 5306; H.R. Kricheldorf, N. Probst, High Perform. Polym. (1995) 7, 471-480). These methods include photocrosslinking of UV sensitive chiral nematic polymers.

A considerable demand exists for cholesteric oligomers with especially thermally crosslinkable end groups whose supermolecular order is not disturbed by crosslinking and which therefore can be crosslinked in the anisotropic phase.

The invention consequently has the objective of developing additional cholesteric oligomers which can be crosslinked in the anisotropic phase, especially thermally, without neutralizing the cholesteric effect.

The subject of the present invention is cholesteric oligomers of formula I



in which

n on the average stands for a value from 0 to 1,

q on the average stands for a value from 0.1 to 2,

p on the average stands for a value of 1 to 20,

A stands for a chiral group,

B stands for a mesogenic group,

$Y^1$ ,  $Y^2$  and  $Y^3$  independently of one another stand for a group of the formula -CO-O-, -O-CO-, or -O-CO-O-,

where the q units ( $A - Y^2 -$ ) and the p units ( $B - Y^3 -$ ) are present in any arbitrary sequence, the q groups A being the same or different and p groups B also being the same or different, and  $Z^1$  and  $Z^2$  independently of one another stand for a group of the formula W-Q-,

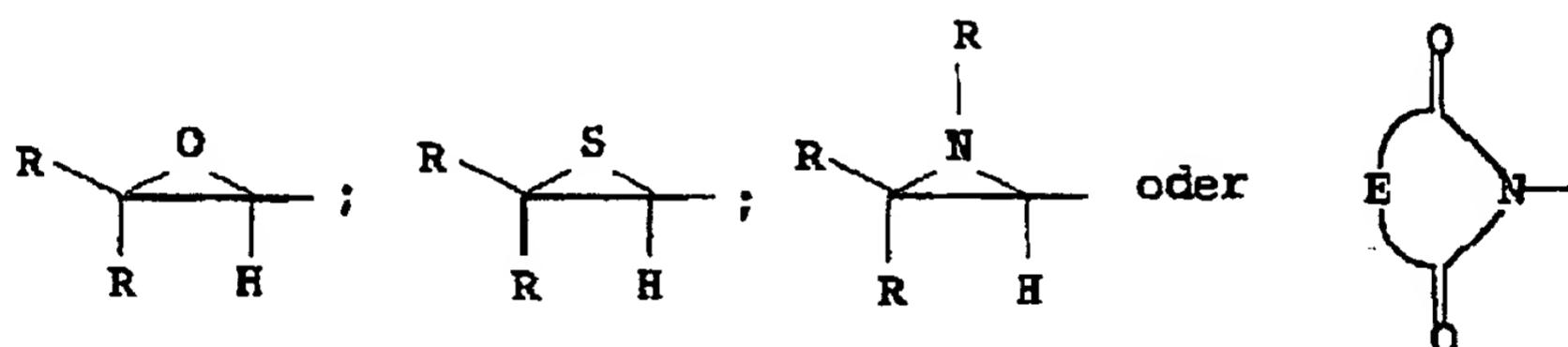
in which

Q stands for a chemical bond or a mono- or polysubstituted alkylene or arylene space, and  
W stands for a crosslinkable heterocyclic group.

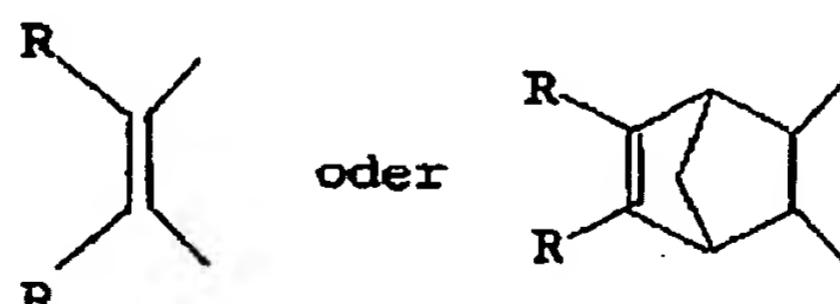
The cholesteric oligomers according to the invention display some surprising advantages:

- a) The oligomers can be crosslinked without destroying the supermolecular order in the anisotropic phase into polymer networks so that the cholesteric effect is permanently fixed.
- b) The polymeric networks are resistant to effects of temperature and weathering.
- c) The initial materials used for production of the oligomers are easily synthesized and purified and therefore readily accessible at reasonable cost.

Preferred cholesteric oligomers are those in which W is selected from among radicals of the formula:



in which E stands for a crosslinkable alkenylene group, and the radicals R are the same or different and denote hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyls, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec.-butyl, or tert.-butyl. E preferably stands for:



oder=or

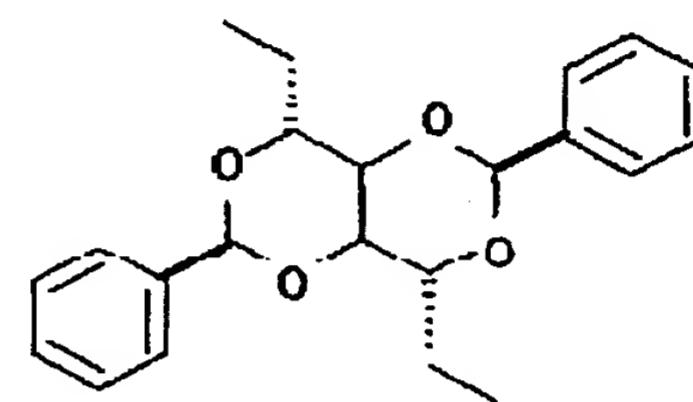
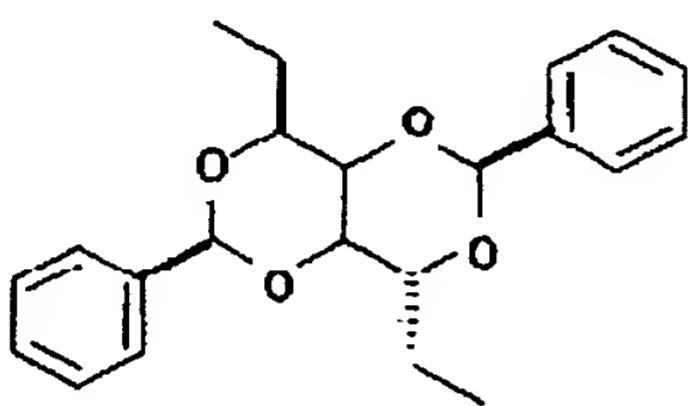
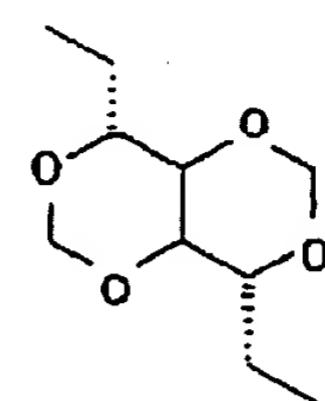
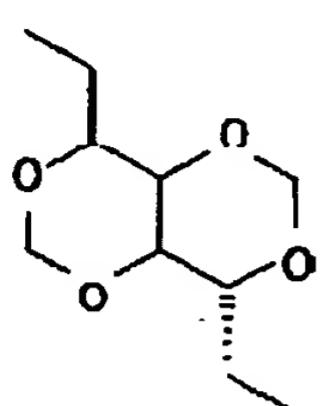
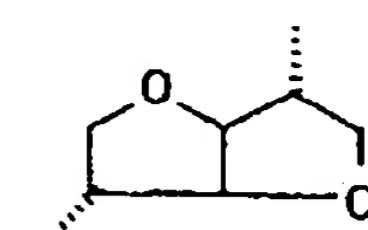
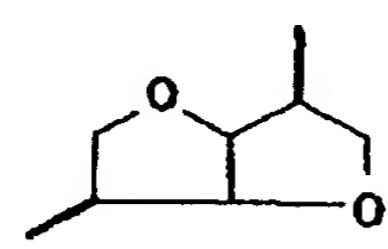
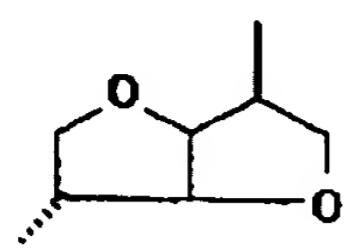
where the radicals R have the above-reported meaning.

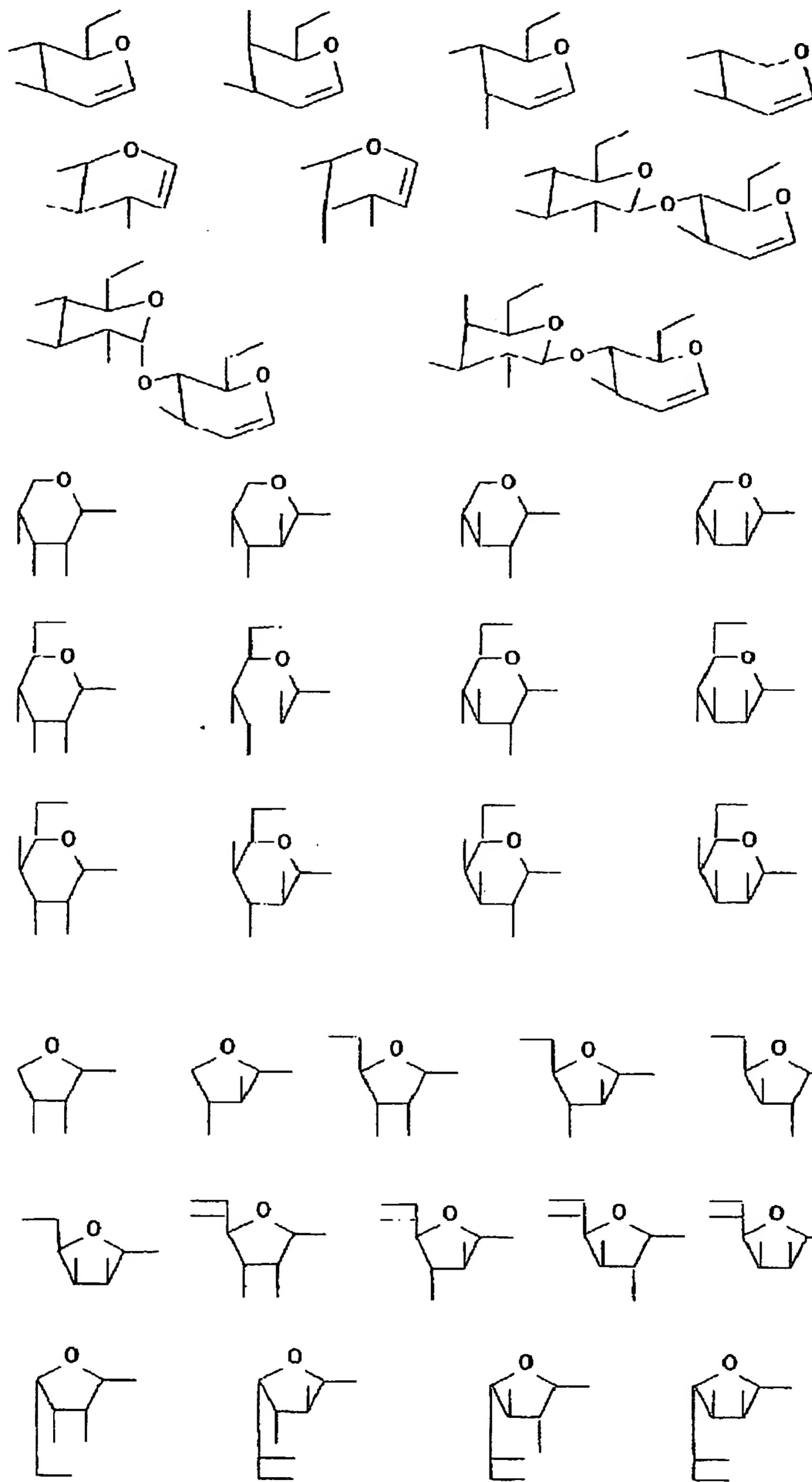
The groups A are preferably selected from among chiral groups which are derived from aliphatic ethers or thio ethers, araliphatic ethers or thioethers, amino acids, especially L-proline, prolinol, camphoric acid or lithocholic acid, resin acids, especially abietic and dehydroabietic acid, sugars, especially pentoses and hexoses, binaphthyl or biphenyl derivatives or from optically active glycols or diols.

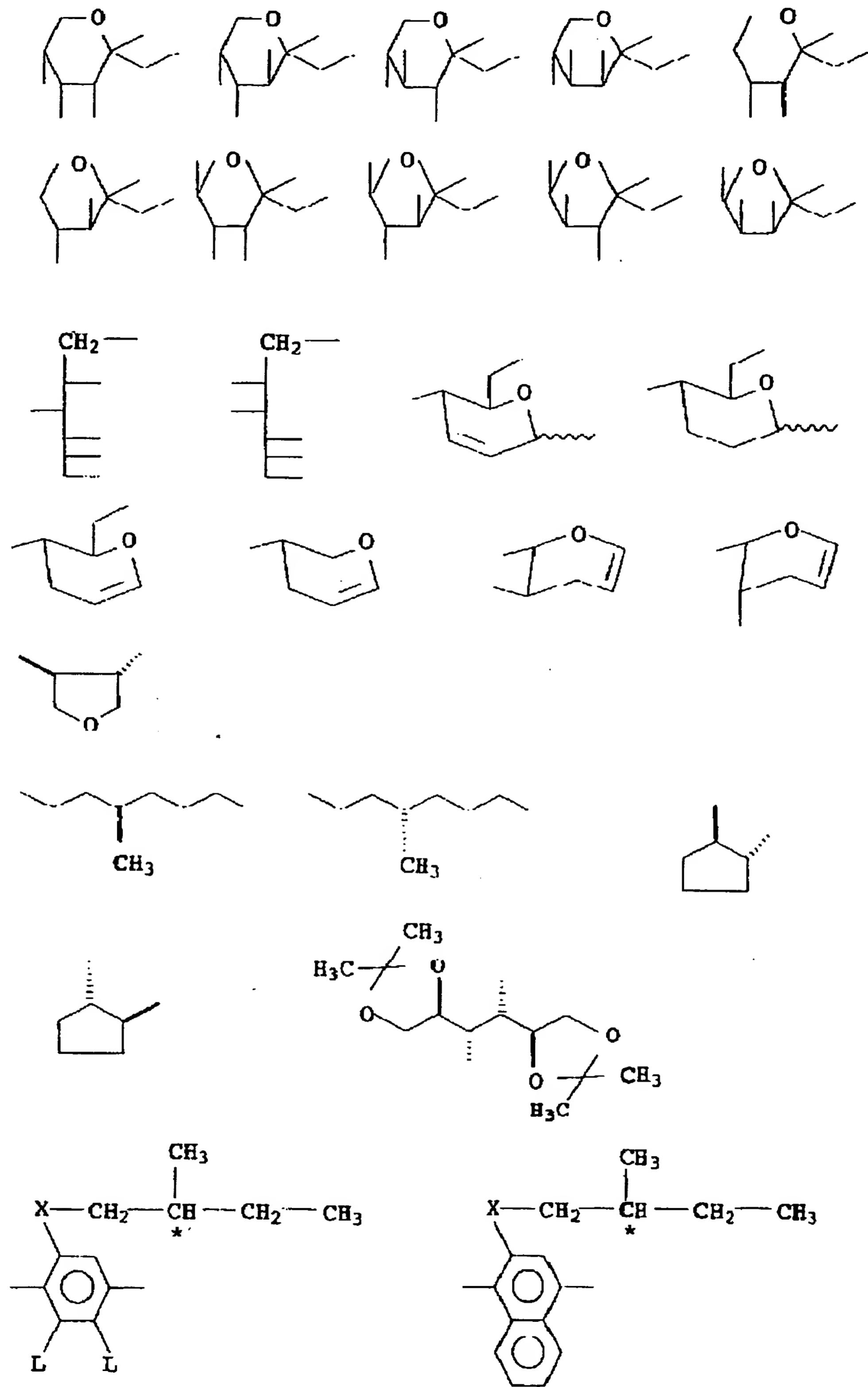
The groups B are preferably selected from among the linear aliphatic, isocycloaliphatic, heterocycloaliphatic, isoaromatic or heteroaromatic groups that are possibly substituted by fluorine, chlorine, bromine, cyano, C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> alkoxy, hydroxy, or nitro, or from among compounds which contain 2 to 4 such groups linked by chemical bonds or by bridge members such as oxygen, sulfur, -CO-O-, -O-CO-O-, -CO-N(R)- or -N(R)-CO-.

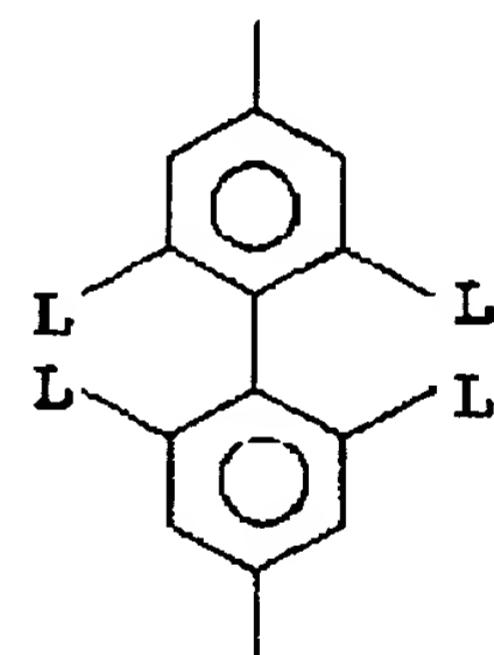
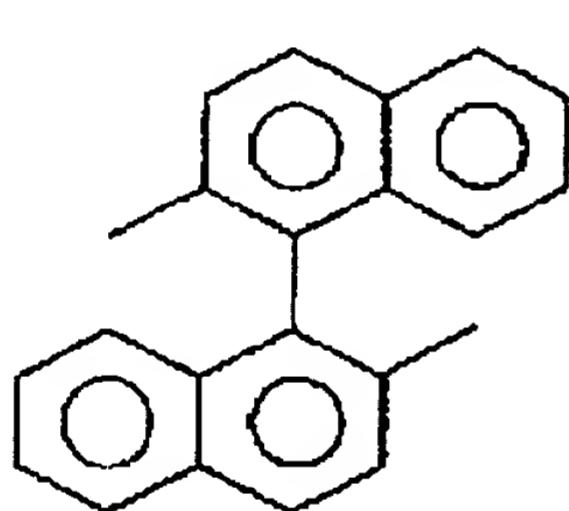
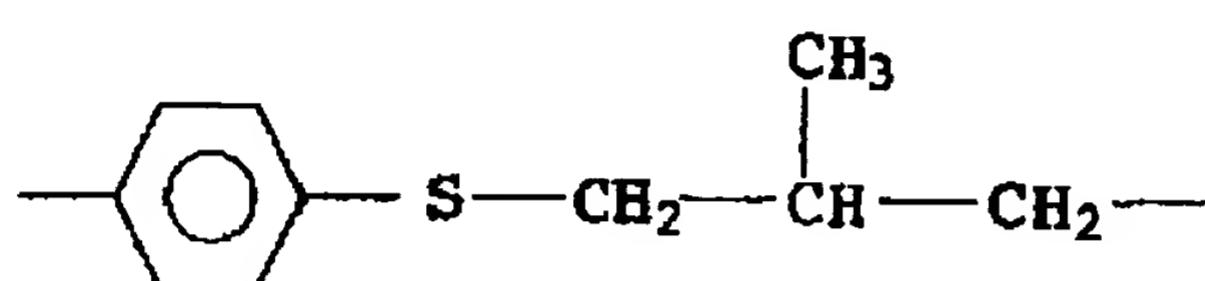
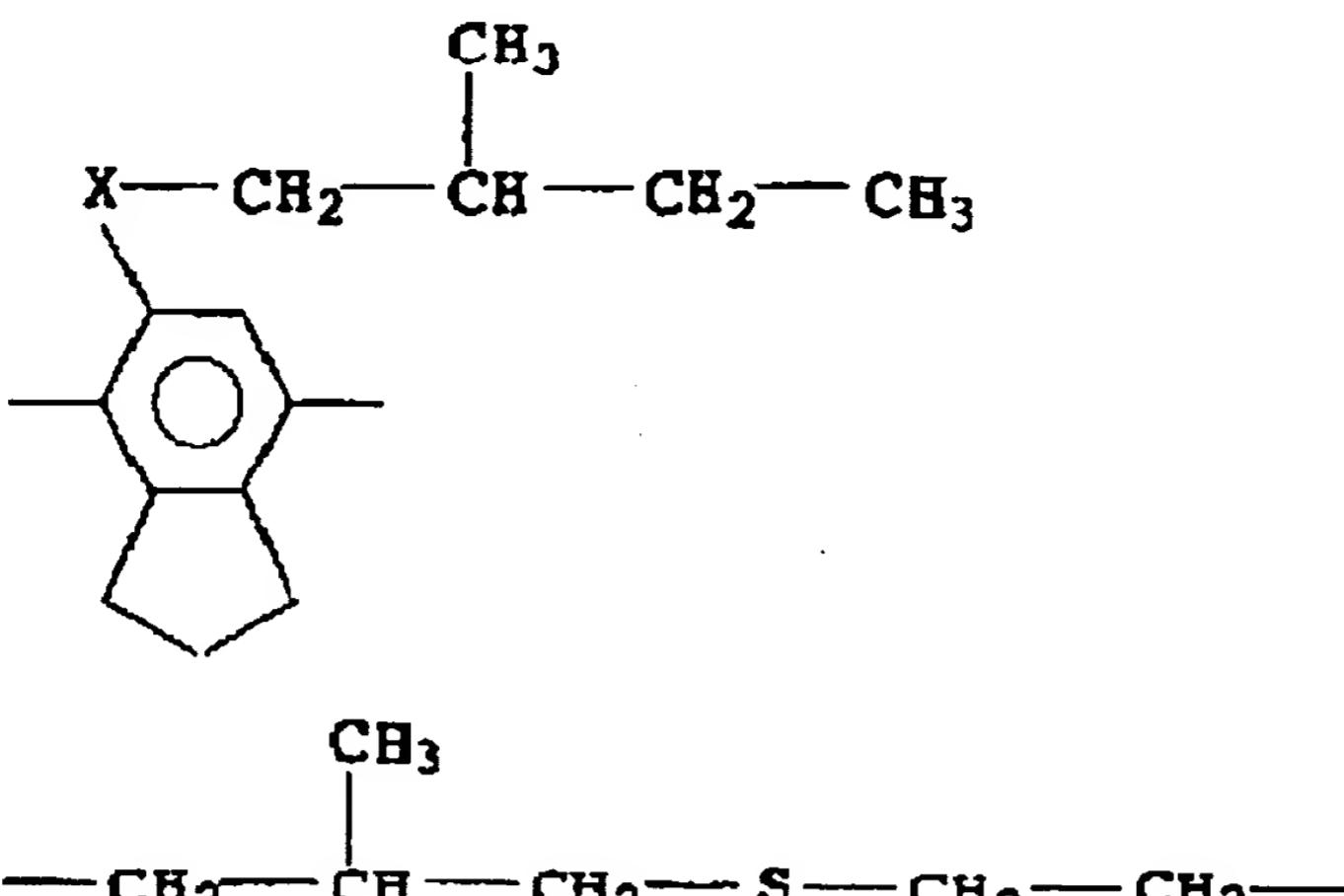
Q preferably stands for a chemical bond or an arylene radical, especially a phenylene or naphthalene radical, possibly substituted with one or more groups selected from C<sub>1</sub>-C<sub>4</sub> alkoxy, fluorine, chlorine, bromine, cyano, hydroxy or nitro.

Especially preferably the groups K are selected independently of one another from groups of the formulas:









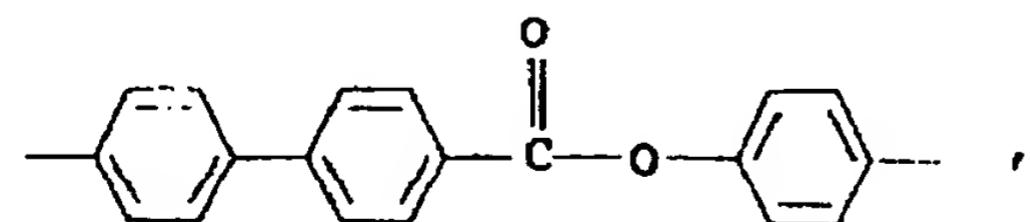
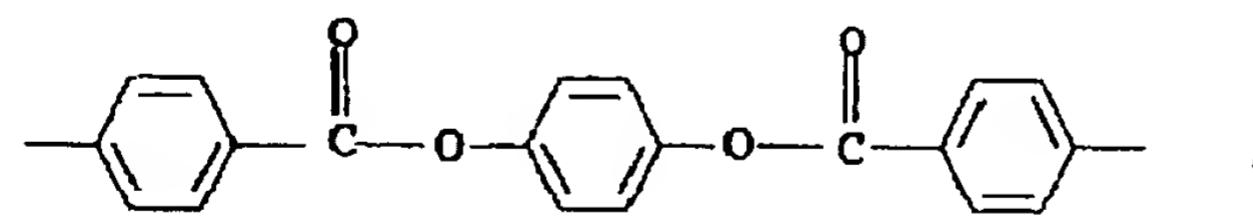
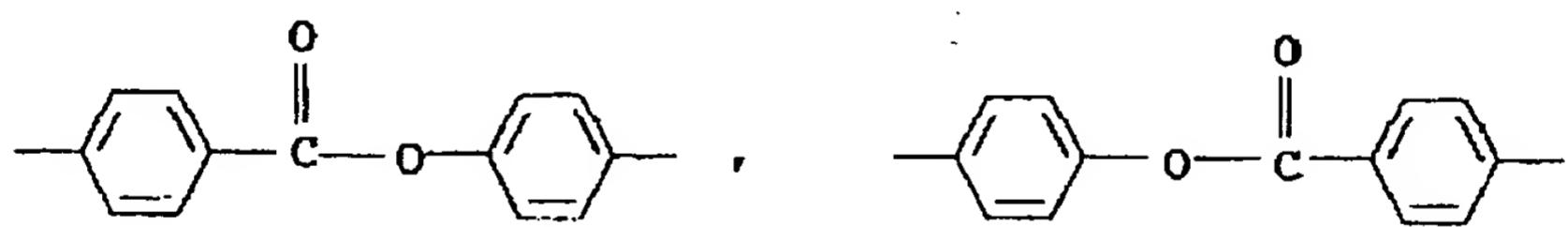
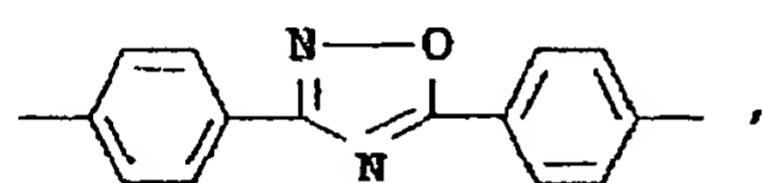
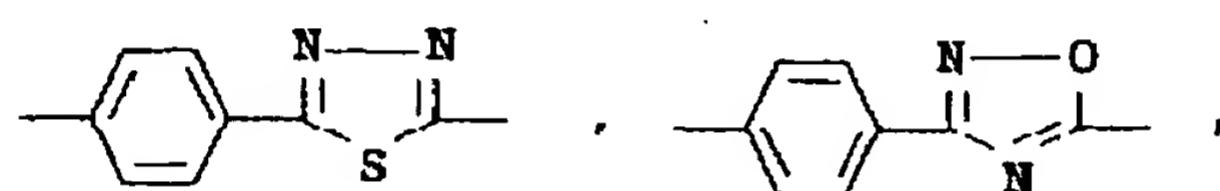
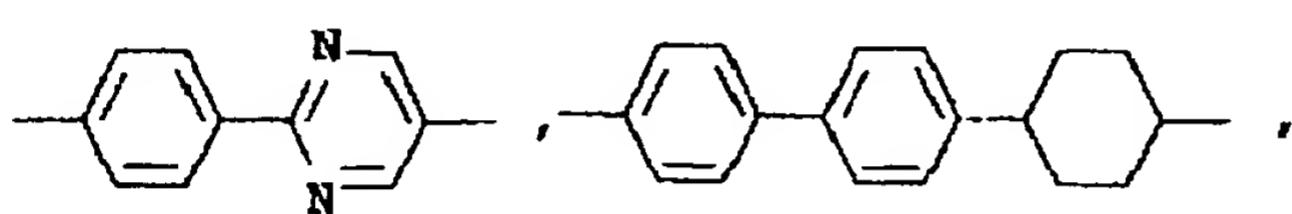
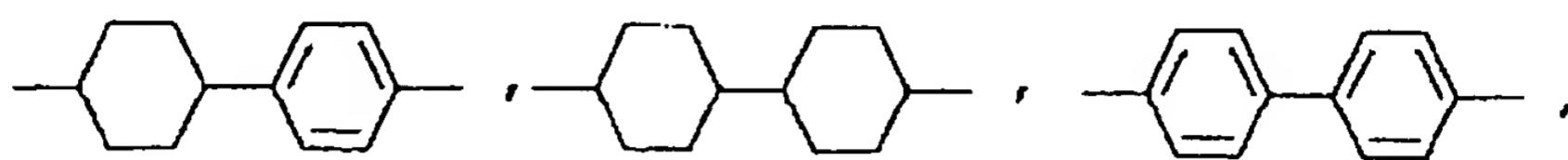
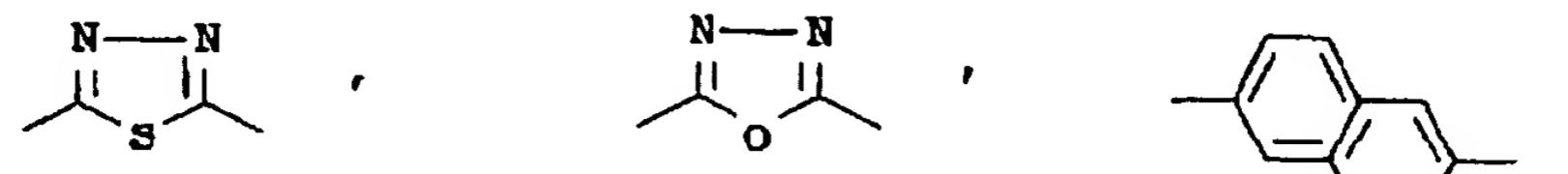
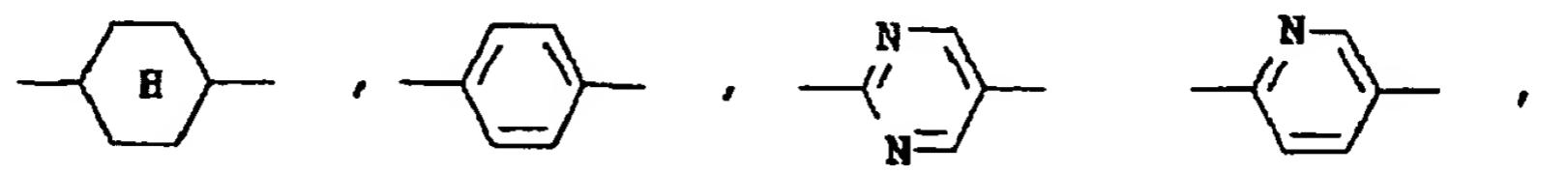
where, in the above formulas:

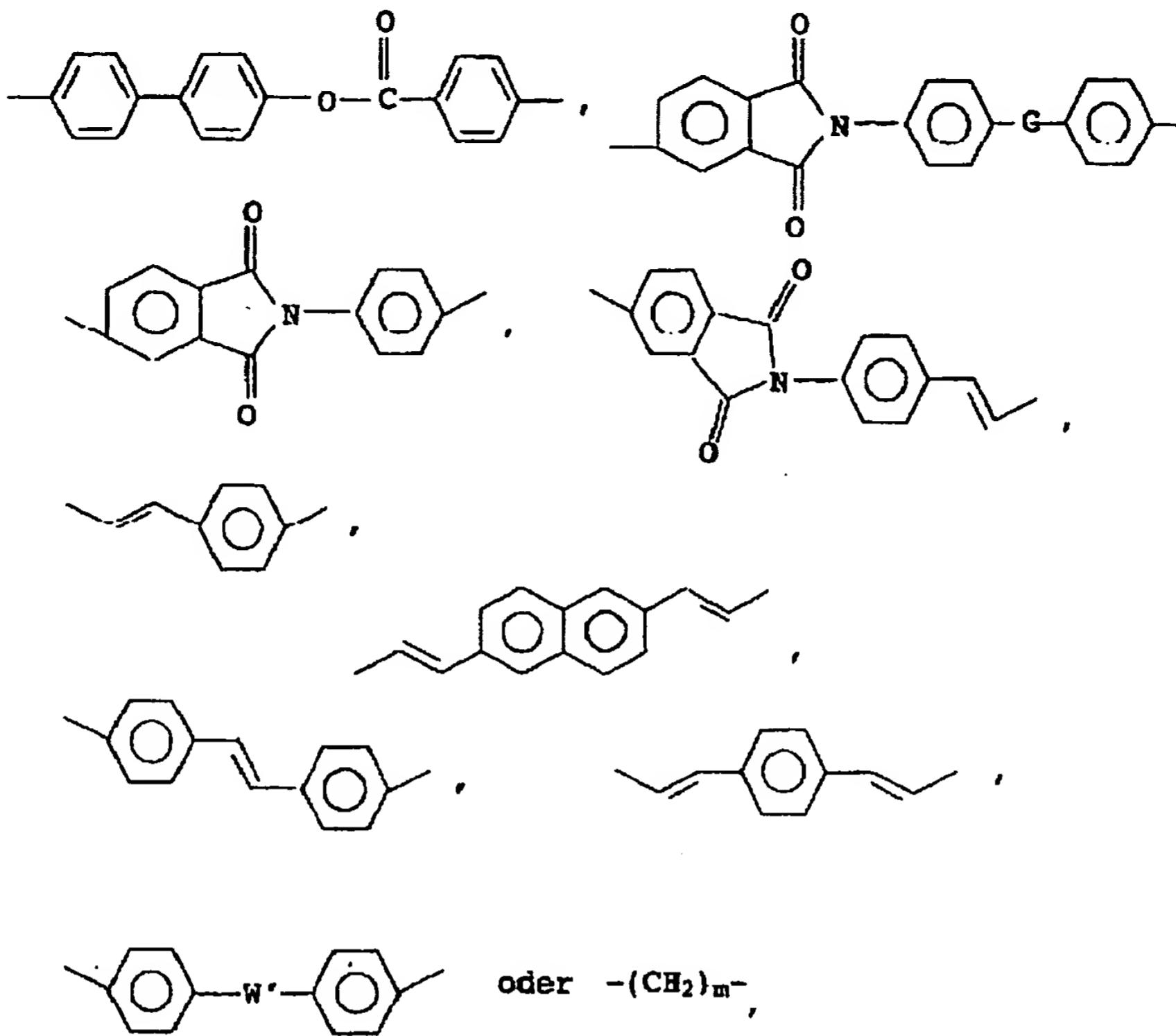
L stands for H, alkyl, alkoxy, alkylthio, halogen, COOR, OCOR, CONHR or NHCOR,

R stands for C<sub>1</sub>-C<sub>4</sub> alkyl or hydrogen, and

X stands for S, O, N, CH<sub>2</sub> or a single bond.

Especially preferably the groups B are selected independently of one another from groups of the formulas:





where each of the phenylene groups or naphthyl groups may display 1, 2 or 3 substituents which independently of one another are selected from among the straight-chained or branched C<sub>1</sub>-C<sub>4</sub> alkyls, C<sub>1</sub>-C<sub>4</sub> alkoxy, fluorine, chlorine, bromine, cyano, hydroxy or nitro, where in the above formulas

W' stands for NR, S, O, (CH<sub>2</sub>)<sub>g</sub>O(CH<sub>2</sub>)<sub>h</sub>, (CH<sub>2</sub>)<sub>m</sub> or O-(CH<sub>2</sub>)<sub>m</sub>-O,

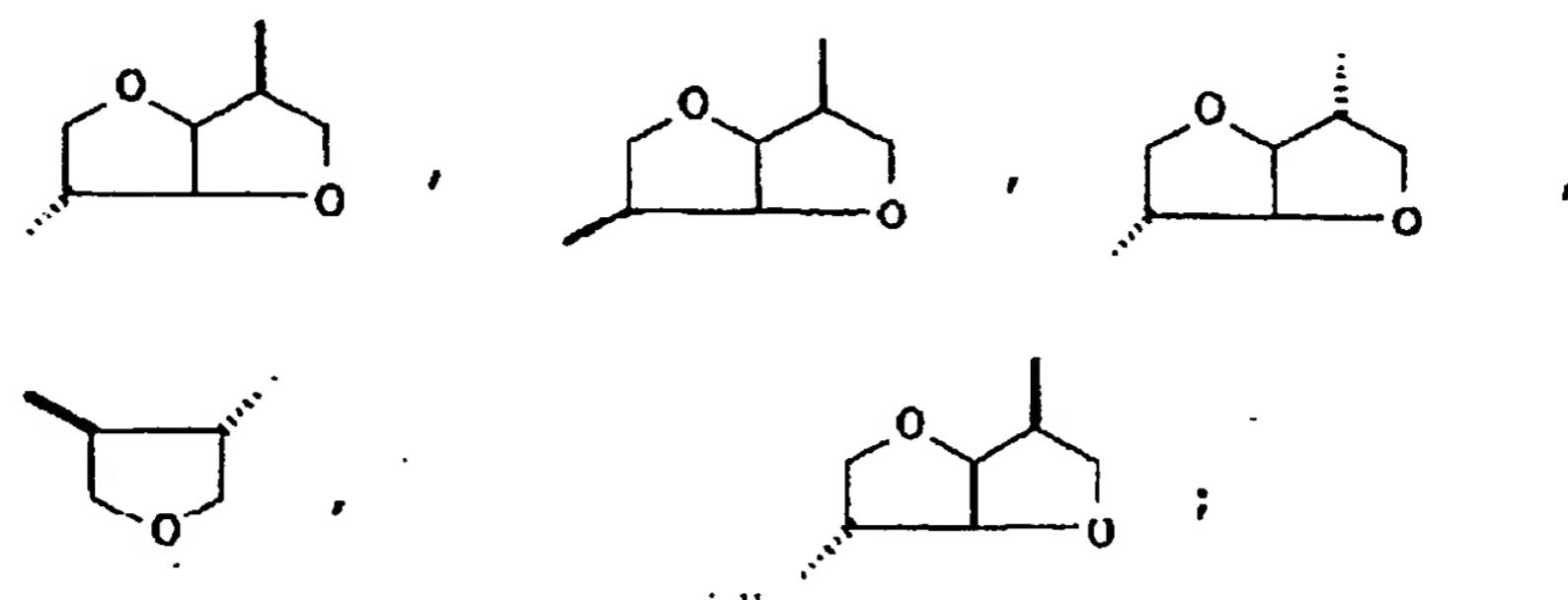
G stands for a single bond, O or S,

R denotes alkyl or hydrogen,

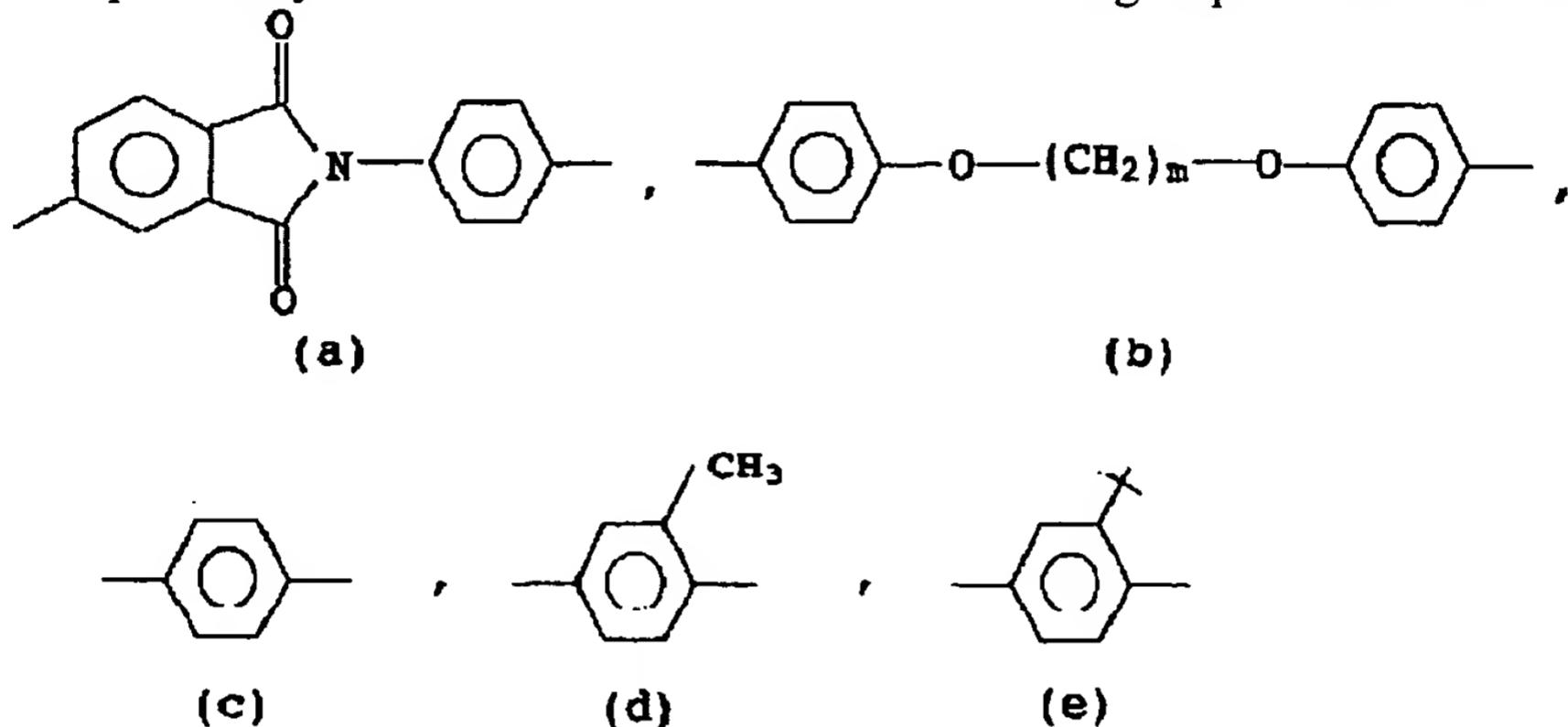
m is a whole number from 1 to 15, and

g and h independently of each other stand for whole numbers from 0 to 10.

Quite especially preferred oligomers according to the invention are those in which the groups A independently of one another are selected from among groups of the formulas:



the groups B independently of one another are selected from the groups of the formulas:



and  $-(CH_2)_m-$  especially (a), (d), and/or (e) where  
(f)

where  $m$  stands for a whole number from 4 to 12,

m stands for a whole number from 4 to 10.

the groups Y independently of one another stand for -CO-O- or -O-CO- and

Z stands for

Preferably in the oligomers according to the invention of formula I q stands for 0.1-1, p for 2 and n for 1

The oligomers according to the invention contain the groups A, B, and Z in the molar ratio of A/B/Z of about 0.05 to 2/approximately 1 to 30/approximately 0.5 to 5, especially from about 0.1 to 1/about 0.5 to 20/about 1.5 to 2.5 condensed in.

The intrinsic viscosity of the cholesteric oligomers is about 0.1-3 dl/g, especially 0.1-1.5 dl/g, especially preferably about 0.1-0.5 dl/g measured at 20 °C with C=2 g/l in dichloromethane/trifluoroacetic acid (volume ratio 4/1). The glass transition point (determined by TLC of the oligomers according to the invention lies approximately in the range from 80 to 300 °C, especially 90-200 °C, especially preferably 90 to 140 °C.

By heating the oligomers according to the invention, preferably at a temperature of about 200-350 °C, especially 250-300 °C cholesteric polymeric networks can be obtained which represent another subject of the present invention.

The synthesis of the cholesteric oligoesters or oligocarbonates according to the invention can be accomplished by various reactions of condensation which are well known to the man of the art, which are known for polyesters among other from H. R. Kricheldorf, N. Probst, Macromol. Rapid Commun. 16, 231 (1995) and N. Probst, H. R. Kricheldorf, High Perform. Polym. 7, 461 (1995) and for polycarbonates from DE-A 196 31 658.

The oligoesters according to the invention are preferably synthesized at elevated temperature but below the crosslinking temperature of the reagents or reaction products, generally in the range from 120 to 250 °C, the temperature in this range also possibly being raised in steps. However it is also possible to produce the oligoesters according to the invention at a lower temperature, e.g., in the range from -10 to +50 °C.

The reaction time may vary in a broad range. It generally amounts to 1-48 h, especially 1 to 24 h.

During the condensation process which is preferred for the production of the oligoesters according to the invention free diols of the formula A-(OH)<sub>2</sub> are brought to reaction with activated dicarboxylic acids, especially dicarboxylic dichlorides of formula B-(COCl)<sub>2</sub> and with groups or radicals of the formula Z-OH and possibly the free diols of the formula B-(OH)<sub>2</sub> in a

suitable inert solvent, especially an inert organic solvent, such as N,N-dimethylacetamide, an ether such as dioxane or tetrahydrofuran, an chlorinated hydrocarbon such as dichloromethane, dichloroethane, 1,1-2,2-tetrachloroethane, 1,2-dichlorobenzene, or especially preferably 1-chloronaphthalene. The chain length of the oligomers according to the invention is adjustable via the quantity of groups or radicals of the formula Z-OH introduced and/or via the time of their addition. Advisably the condensation is conducted in the presence of a base such as pyridine, N-methylmorpholine, or a trialkylamine, especially triethylamine as a HCl acceptor. As the reaction vessel, for example, a pressure resistant agitator container with gas inlet and outlet lines is suitable. Preferably one works under nitrogen. The oligoester obtained is dried at elevated temperature, e.g., at 80 °C in the vacuum. If necessary, the oligoester is subjected to purifying step by redissolving it in one of the above-mentioned solvents and precipitating it out with methanol. If the oligomer is soluble in the solvent used, the organic phase is removed, and the oligoester is obtained from it in the usual way, e.g., by absorption in methanol and filtration. If the oligomer, conversely, precipitates out of the solvent or if gel formation occurs, the reaction mixture is diluted, if necessary, e.g. with methanol, and the oligomer is filtered off.

The oligocarbonates according to the invention are synthesized generally at a reaction temperature lying in the range from 0 °C to ambient temperature. However, it may also be higher, especially in order to complete the reaction. The reaction time is variable over a broad range; it generally amounts to 10 minutes to 24 hours, especially 10 minutes to 5 hours.

In the preferred condensation process for the production of the oligocarbonates according to the invention groups of the formulas A-(OH)<sub>2</sub> and B-(OH)<sub>2</sub> are dissolved in an amine, preferably a tertiary or aromatic amine, such as pyridine or triethylamine. Groups or radical of the formulas Z-(OH) are dissolved in the same solvent, either separately from the diols or together with them. Phosgene, diphosgene, or triphosgene is dissolved in a suitable organic

solvent, such as an ether, e.g., tetrahydrofuran or dioxane, a chlorinated hydrocarbon such as dichloromethane, 1,1-2,2-tetrachloroethane, 1-chloronaphthalene, chlorobenzene or 1,2-dichlorobenzene. This solution is added to the solution containing the diols and possibly the groups or radicals of formulas Z-OH. If the groups or radicals of formulas Z-OH are not dissolved together with the diols, then the Z-OH-containing solution is added to the ongoing condensation reaction. The chain length of the oligomers according to the invention is adjustable via the quantity of groups or radicals of the formula Z-OH utilized and/or by the time of addition. If the oligomer is soluble in the solvent used, the organic phase is removed, and the oligocarbonate is obtained from it in the usual way, e.g., by absorption in methanol and filtration. If the oligomer, conversely, precipitates out of the solvent or if gel formation occurs, the reaction mixture is diluted, if necessary, e.g., with methanol, and the oligomer filtered off. Alternatively to phosgene, diphosgene or triphosgene, the chlorinated carbonic acid esters or carbonic acid diesters of the alcohols or diols to be condensed may be used.

The oligomers according to the invention contain the groups A and B in a statistical distribution.

The cholesteric oligomers according to the invention are especially applicable as surface coating material or for the production of pigments.

Pigments can be produced in the usual way by application of the cholesteric oligomer according to the invention to a surface by means of one of the current application procedures (blading, pouring, spraying etc., optionally reorientation of the oligomer film, crosslinking of the oligomer film, detachment of the oriented crosslinked film from the surface and grinding it into flakelike pigments. Single layer or multilayer pigments containing the cholesteric oligomers according to the invention or the cholesteric polymer networks according to the invention are therefore another subject of the present invention.

The cholesteric polymer networks according to the invention or the pigments according to the invention may especially be used in the vehicle and vehicle accessory sector, in EDP, in leisure time and athletic and game sector, as optical structural components, such as polarizers or filters, in the cosmetic sector, in the textile, leather or jewelry sector, in the gift sector, in writing utensils or on eyeglass frames, in the construction sector, in the domestic sector and in printing products of all types and for the production of paints and enamels. The coloring effects achievable with the cholesteric polymeric networks or pigments according to the invention, because of the large number of attainable reflection wavelengths, also include the UV and IR ranges and naturally also the range of visible light.

If the pigments according to the invention are applied to banknotes, checks, other means of legal tender, or passes, e.g. by known printing processes, or incorporated in them, this makes identical copying difficult, especially the counterfeiting of said articles. Another subject of the present invention is therefore the use of the polymeric networks or pigments according to the invention for the treatment of articles to make counterfeiting difficult, especially banknotes, checks or other forms of legal tender or passports. Another subject of the present invention is the use of the polymeric networks or pigments according to the invention for coating articles of general use and for enameling vehicles.

Another subject of the present invention is compositions, especially coating compositions, paints, or enamels which contain the pigments according to the invention.

The compositions according to the invention generally contain, besides the pigments according to the invention the conventional flow promoters, binders and one or more substances selected from among the water-based enamels, e.g., in the form of aqueous dispersion, such as PMA, SA, polyvinyl derivatives, PVC, polyvinylidene chloride, SB-copo, PV-AC-copo resins, or in the form of water-soluble binders such as shellac, maleic resins, colophon-modified phenol

resins, linear and branched, saturated polyesters, aminoplastic-crosslinking, saturated polyesters, fatty acid modified alkyd resins, plasticized urea resins or in the form of water-dilutable binders such as PUR dispersion, EP resins, urea resins, melamine resins, phenol resins, alkyd resins, alkyd resin emulsion, silicone resin emulsions, powdered enamels such as powdered enamels for TRIBO/ES such as polyester coating powder resins, PUR coating powder resins, EP coating powder resins, EP/SP hybride coating powder resins, PMA coating powder resins, or powder enamels for eddy current/vortex sintering, such as thermoplasticized EPS, LD-PE, LLD-PE, HD-PE, solvent-containing enamels, such as a single or two-component enamel (binder), such as shellac, colophon resin ester, maleinate resins, nitrocelluloses, colophon-modified phenol resins, physically drying saturated polyesters, aminoplastic-crosslinking saturated polyester, isocyanate-crosslinking saturated polyesters, self-crosslinking saturated polyesters, alkyds with saturated fatty acids, linseed oil alkyd resins, soybean oil resins, sunflower seed oil alkyd resins, safflower oil alkyd resins, ricinene alkyd resins, wood oil/linseed oil alkyd resins, mixed oil alkyd resins, resin-modified alkyd resins, styrene/vinyltoluene-modified alkyd resins, acrylated alkyd resins, urethane-modified alkyd resins, silicone-modified alkyd resins, epoxide-modified alkyd resins, isophthalic acid alkyd resins, nonplasticized urea resins, plasticized urea resins, melamine resins, polyvinylacetals, non-crosslinking P(M)A-homo- or co-polymers, non-crosslinking P(M)A homo- or co-polymers with non-acrylic monomers, self-crosslinking P(M)A homo- or copolymers, P(M)A-copolymers with other non-acrylic monomers, foreign-crosslinking P(M)A homo- or copolymers, foreign-crosslinking P(M)A copolymers with non-acrylic monomers, acrylate copolymerization resins, unsaturated hydrocarbon resins, organic soluble cellulose compounds, silicone combination resins, PUR resins, P resins, peroxide hardening, unsaturated synthetic resins, radiation-hardening synthetic resins, photoinitiator-containing radiation-hardening synthetic resins, photoinitiator-free, solvent-free enamels (binders) such as isocyanate-

crosslinking saturated polyesters, PUR-2K resin systems, PUR-1K resin systems, moisture-hardening, EP resins, and synthetic resins -- individually or in combination -- such as acrylonitrile-butadiene-styrene copolymers, BS, cellulose acetate, cellulose acetobutyrate, cellulose acetopropionate, cellulose nitrate, cellulose propionate, artificial horn, epoxy resins, polyamide, polycarbonate, polyethylene, polybutylene terephthalate, polyethylene terephthalate, polymethylmethacrylate, polypropylene, polystyrene, polytetrafluoroethylene, polyvinylchloride, polyvinylidenechloride, polyurethane, styrene-acrylonitrile polymers, unsaturated polyester resins, as granulates, powders or powders as casting resins.

The composition according to the invention may also contain stabilizers against UV and weather factors as well as additional inorganic or organic pigments.

The pigments according to the invention may be incorporated individually or in mixtures in the compositions according to the invention and there optionally be aligned by methods triggering shearing forces. Suitable methods for aligning the pigments according to the invention include pressing or blading.

Both the coating of surfaces with the cholesteric oligomers according to the invention and also the coating of articles of everyday use with compositions according to the invention can be accomplished by conventional surface coating processes such as blade coating, airbrushing, squeeze coating, impregnation coating, reverse roller coating, transfer roll coating, "kiss coating," spray coating, spin coating, or pour coating, as described in DE-A 197 40 181. Other suitable surface-coating processes are conventional printing processes (such as high, deep, flexo, offset or screen printing) which are described, for example, in WO 96/02597 and which are referred to here in their full scope.

The following examples illustrate the invention without limiting it.

The physical properties of the compounds described in the examples are reported in Table 1-3.

### Examples

The monomers shown in Diagram 1 were dissolved in the quantities reported in Diagram 2 in 20 ml of 1-chloronaphthalene and added to a cylindrical glass reactor equipped with a mechanical agitator and gas inlets and outlets. The reaction vessel was placed in an oil bath preheated to 120 °C, and the temperature was rapidly raised to 200 °C. The reaction mixture was stirred under nitrogen for 6 hours at 200 °C. After cooling the reaction product was dissolved in dichloromethane/trifluoroacetic acid (volume ratio 4:1), precipitated in methanol and dried in the vacuum at 80 °C.

In this way 16 cholesteric oligoesters were prepared which could be crosslinked thermally in the anisotropic phase.

**Diagram 1.** Structural formulas of the monomers used (Me stands for methyl)

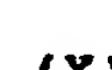
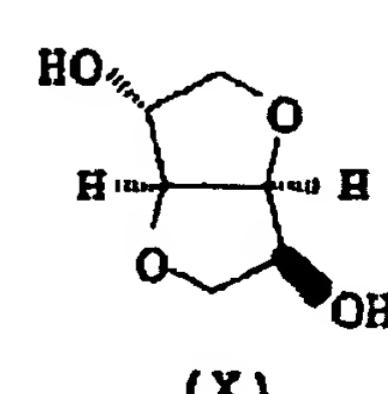
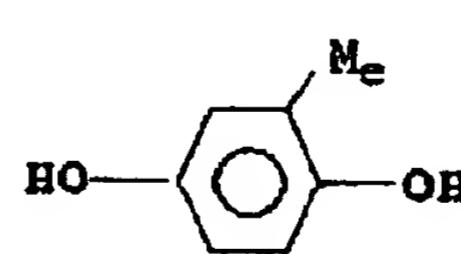
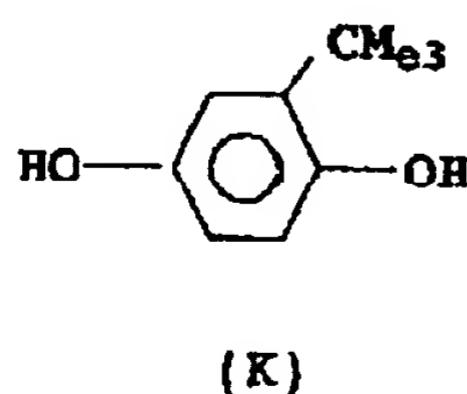
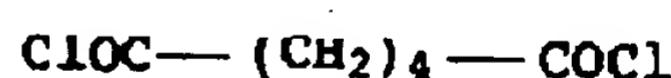
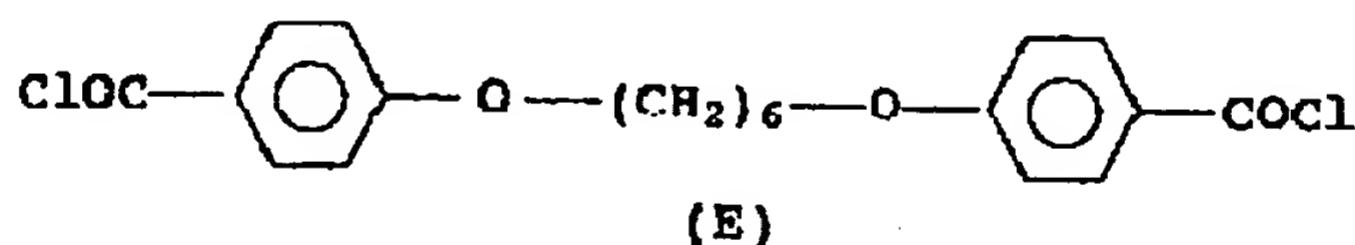
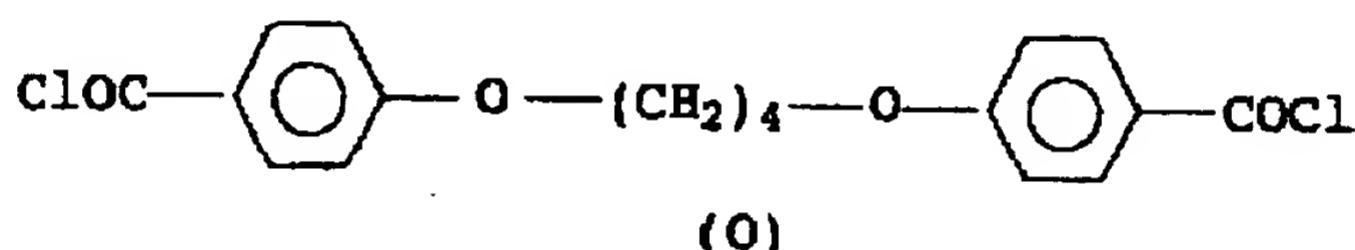
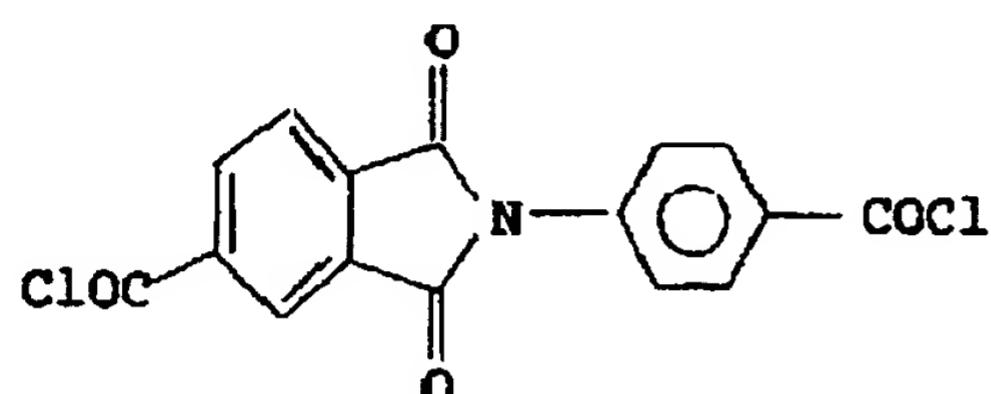
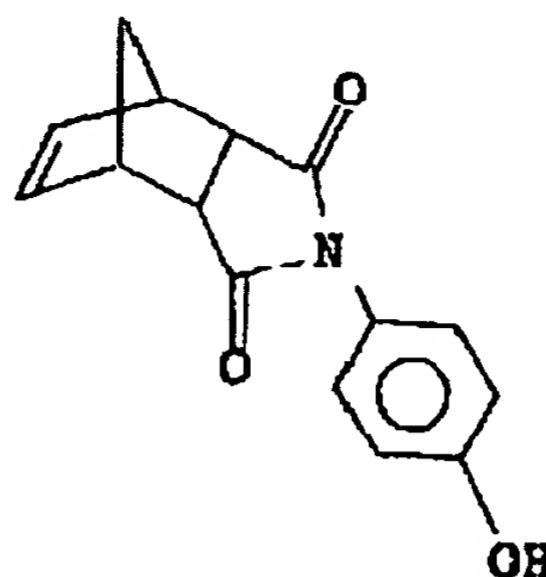
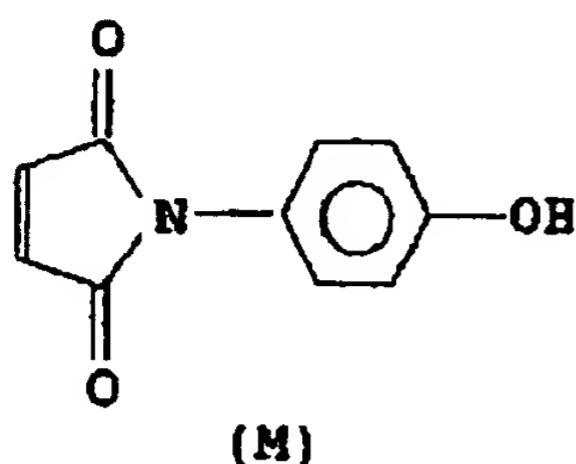


Diagram 2. Usage quantities (in mmole) of the monomers used

Oligomer 1:	10 M + 40 C + 15 E +	45 K +	5 X
Oligomer 2:	10 M + 20 C + 10 E +	25 K +	2,5 X
Oligomer 3:	10 M + 20 C + 10 E +	23,75 K +	1,25 X
Oligomer 4:	10 M + 10 C + 5 E +	9,375 K +	0,625 X
Oligomer 5:	10 M + 20 C + 10 O +	23,75 K +	1,25 X
Oligomer 6:	10 M + 10 C + 5 O +	9,375 K +	0,625 X
Oligomer 7:	10 M + 20 C + 20 H +	32,5 K +	2,5 X
Oligomer 8:	10 M + 10 C + 10 H +	14,375 K +	0,625 X
Oligomer 9:	10 M + 20 C + 10 O +	23,75 L +	1,25 X
Oligomer 10:	10 M + 10 C + 5 O +	9,375 L +	0,625 X
Oligomer 11:	10 M + 20 C + 10 J +	23,75 K +	1,25 X
Oligomer 12:	10 M + 10 C + 5 J +	9,375 K +	0,625 X
Oligomer 13:	10 N + 20 C + 10 O +	23,75 L +	1,25 X
Oligomer 14:	10 N + 10 C + 5 O +	9,375 L +	0,625 X
Oligomer 15:	10 N + 20 C + 20 H +	32,5 L +	2,5 X
Oligomer 16:	10 N + 10 C + 10 H +	14,375 L +	0,625 X

**Table 1. Yield and properties of oligo(ester)imides with maleimide end groups**

Oligomer No.	Yield (%)	<sup>a)</sup> int	T <sub>g</sub> <sup>b)</sup>	T <sub>i</sub> <sup>c)</sup>	Texture	Crosslinking
1	93	0115	130	310-325	cholesteric	in the LC phase at 250 C after 1 h
2	96	0.15	126	360-370 190-220 C	GJ blue	in the chol. phase at 250 C (30 min)
3	97	0.14	125	350-370 190-230 C, then chol.	GJ blue/green	in the chol. phase at 250 C (30 min)
4	95	0.10	101	380-390	chol. at 180 C	in the chol. phase at 250 C (30 min)
5	98	0,17	121	>400 200-260 C	GJ orange/yellow	in the chol. phase at 250 C (30 min)
6	96	0.14	115	>400 chol. at 190 C		in the chol. phase at 250 C (30 min)
7	98	0.20	118	>400 190-270 C	GJ blue	in the GJ texture at 250 C (30 min)
8	97	0.11	118	>400 200-260 C	GJ yellow/green	in the GJ texture at 250 C (30 min)

a) Measured at 20 C with c = 2 g/l in CH<sub>2</sub>Cl<sub>2</sub>/trifluoroacetic acid (volume ratio 4:1)

b) TLC measurement, heating rate 20 C/min.

c) optic microscope, heating rate 10 C/min

**Table 2. Yield and properties of oligoesters with maleimide end groups**

Oligomer No.	Yield (%)	int <sup>a)</sup>	T <sub>g</sub> <sup>b)</sup>	T <sub>i</sub> <sup>c)</sup>	Texture	Crosslinking
9	96	0.18	107	>400	GJ blue at 260 C	in the GJ texture at 250 C (10 min)
10	95	0.17	106	>400	GJ green/yellow at 230-320 C	in the GJ texture at 250 C (30 min), at 300 C (5 min)
11	94	0.13	109	300-310	GJ blue after shearing, otherwise chol.	in the chol. phase at 250 C (30 min)
12	96	0.17	129	290-300	chol. at 200 C	in the chol. phase at 250 C (15 min)

a) Measured at 20 C with c = 2 g/l in CH<sub>2</sub>Cl<sub>2</sub>/trifluoroacetic acid (volume ratio 4:1)

b) TLC measurement, heating rate 20 C/min.

c) optic microscope, heating rate 10 C/min

**Table 3. Yield and properties of oligoesters with norbornene dicarboxylic acid imide end groups**

Oligomer No.	Yield (%)	<sup>a)</sup> int	T <sub>g</sub> <sup>b)</sup>	T <sub>i</sub> <sup>c)</sup>	Texture	Crosslinking
13	98	0.20	107	>400	GJ yellow at 220 C	in the GJ texture at 300 C (5 min)
14	97	0.14	95	>400	GJ orange/red at 230 C	in the GJ texture at 300 C (5 min)
15	98	0.17	130	>400	GJ light blue at 220 C	in the GJ texture at 300 C (5 min)
16	96	0.19	130	>400	GJ orange at 220 C	in the GJ texture at 300 C (5 min)

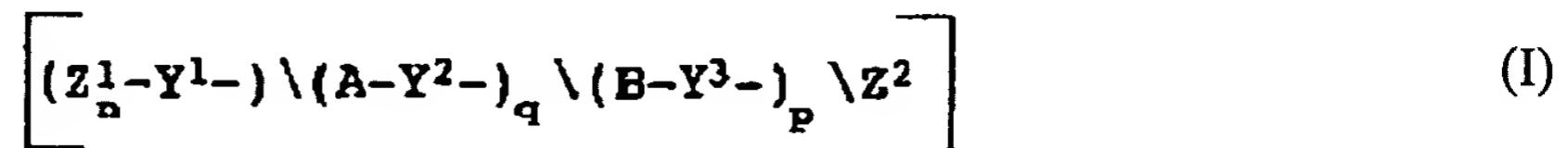
a) Measured at 20 C with c = 2 g/l in CH<sub>2</sub>Cl<sub>2</sub>/trifluoroacetic acid (volume ratio 4:1)

b) TLC measurement, heating rate 20 C/min.

c) optic microscope, heating rate 10 C/min

## Claims

1. Cholesteric oligomers of formula I



in which

n on the average stands for a value from 0 to 1,

q on the average stands for a value from 0.1 to 2,

p on the average stands for a value of 1 to 20,

A stands for a chiral group,

B stands for a mesogenic group,

$Y^1$ ,  $Y^2$  and  $Y^3$  independently of one another stand for a group of the formula -CO-O-, -O-CO-, or -O-CO-O-,

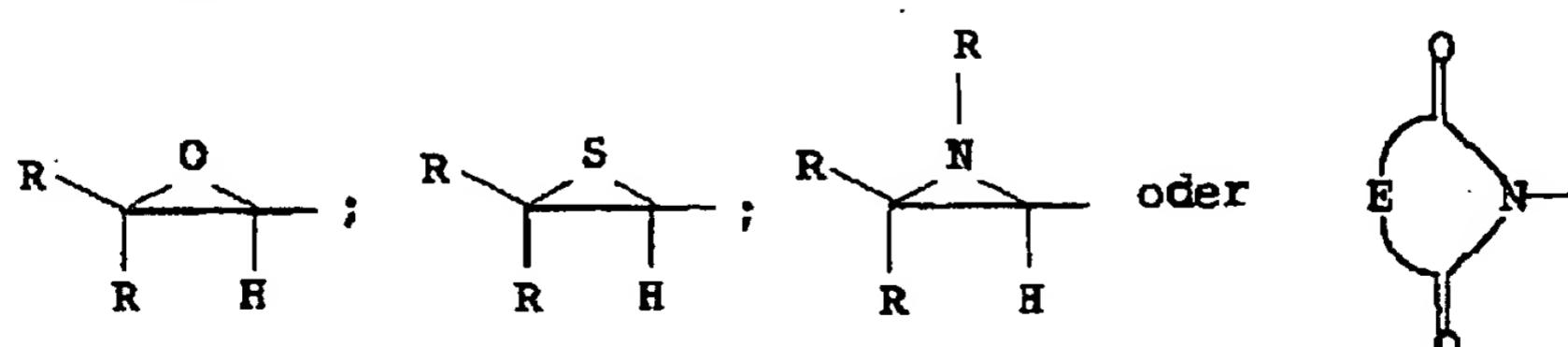
where the q units ( $A - Y^2 -$ ) and the p units ( $B - Y^3 -$ ) are present in any arbitrary sequence, the q groups A being the same or different and p groups B also being the same or different, and  $Z^1$  and  $Z^2$  independently of one another stand for a group of the formula W-Q-,

in which

Q stands for a chemical bond or a mono- or polysubstituted alkylene or arylene space, and

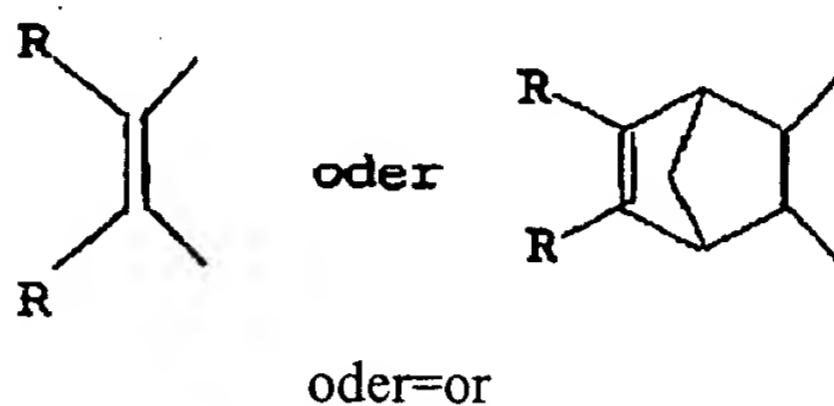
W stands for a crosslinkable heterocyclic group.

2. Cholesteric oligomers as in claim 1 characterized by the fact that W is selected from radicals of the formula



in which E stands for a crosslinkable alkenylene group, and the radicals R are the same or different and denote hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyls, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec.-butyl, or tert.-butyl.

3. Cholesteric oligomers as in claim 1 characterized by the fact that E stands for



oder=or

where the radicals R have the above-reported meaning.

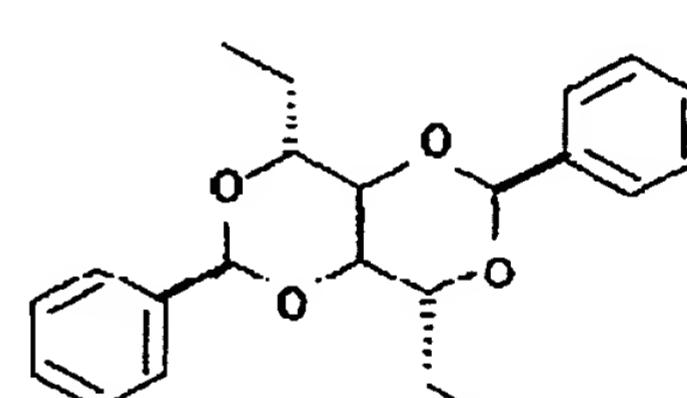
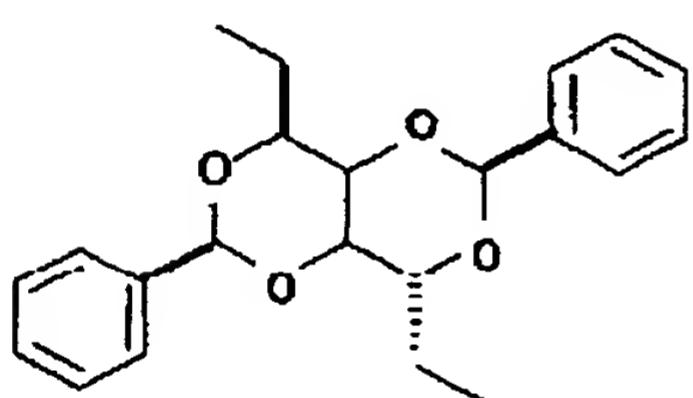
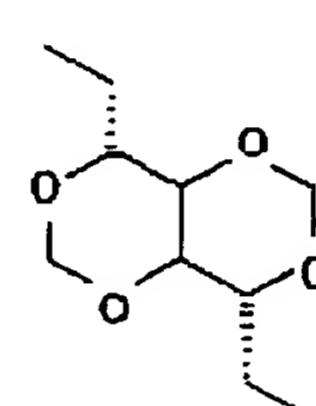
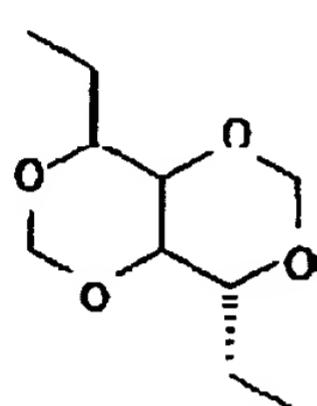
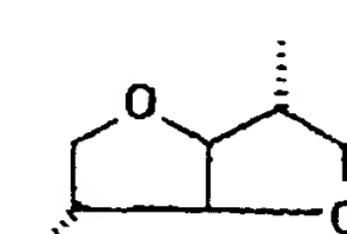
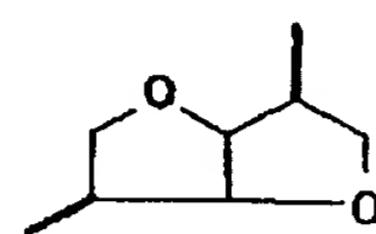
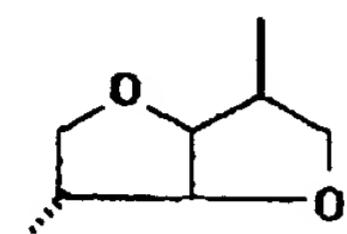
4. Cholesteric oligomers as in claim 1 in which the groups A are selected from among chiral groups which are derived from aliphatic ethers or thio ethers, araliphatic ethers or thioethers, amino acids, especially L-proline, prolinol, camphoric acid or lithocholic acid, resin acids, especially abietic and dehydroabietic acid, sugars, especially pentoses and hexoses, binaphthyl or biphenyl derivatives or from optically active glycols or diols;

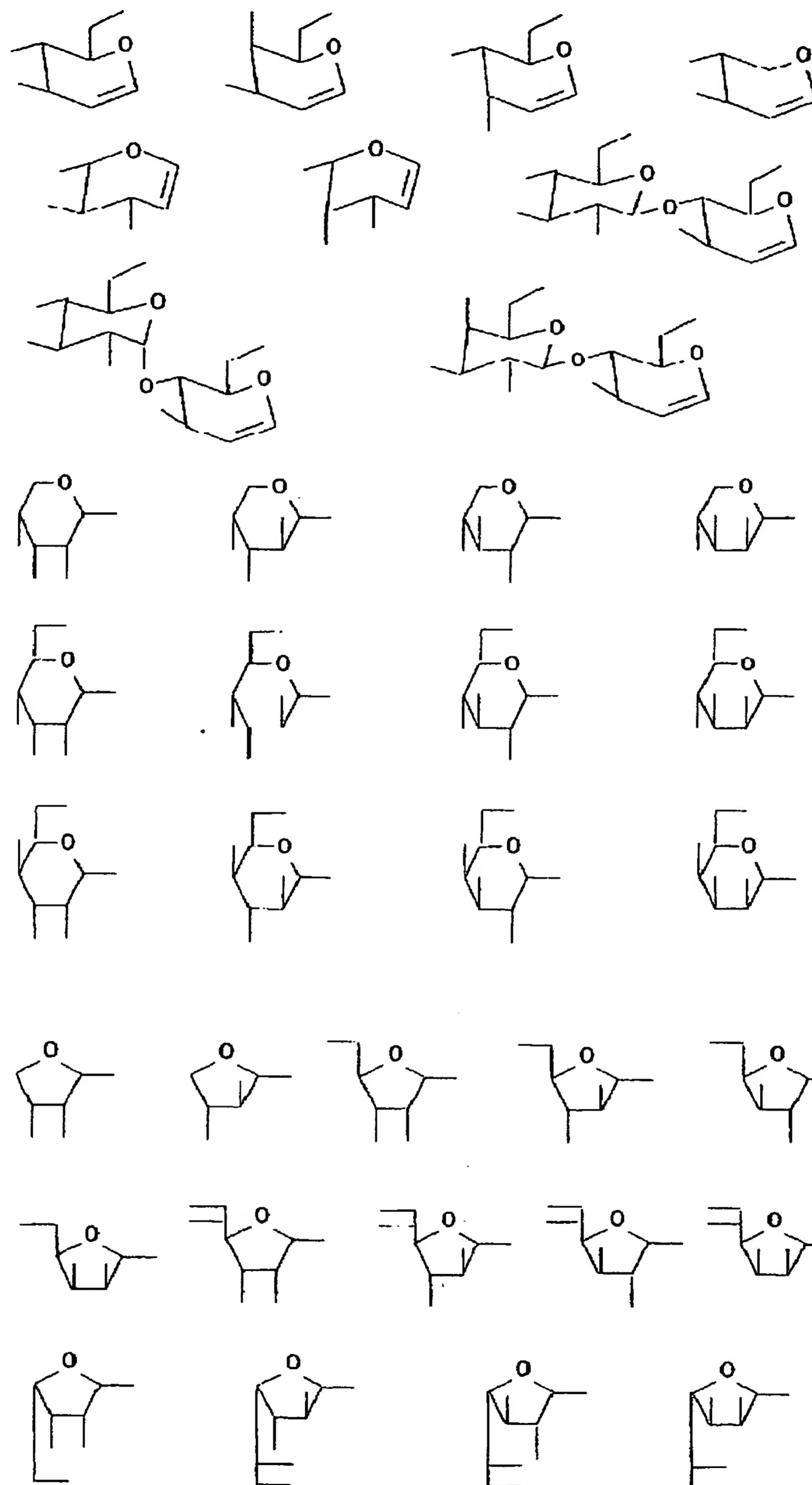
the groups B are selected from among the linear aliphatic, isocycloaliphatic, heterocycloaliphatic, isoaromatic or heteroaromatic groups that are possibly substituted by fluorine, chlorine, bromine, cyano, C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> alkoxy, hydroxy, or nitro, or from among compounds which contain 2 to 4 such groups linked by chemical bonds or by bridge members such as oxygen, sulfur, -CO-O-, -O-CO-O-, -CO-N(R)- or -N(R)-CO-, and

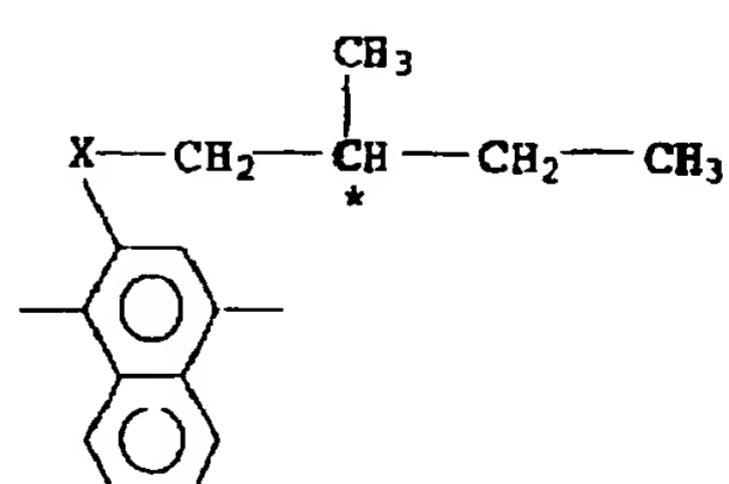
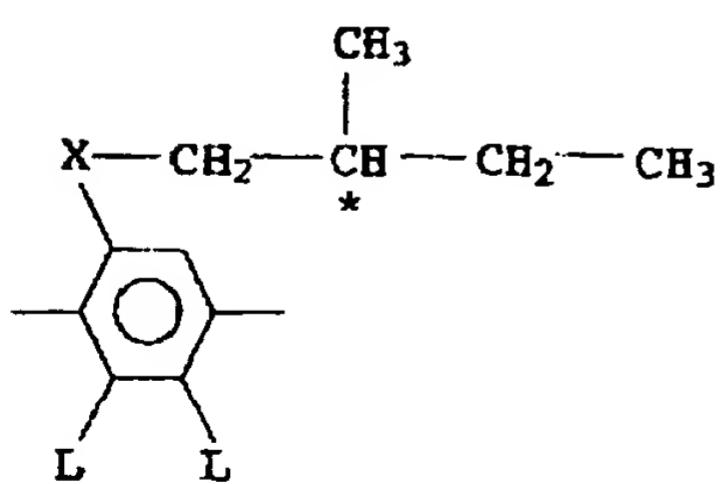
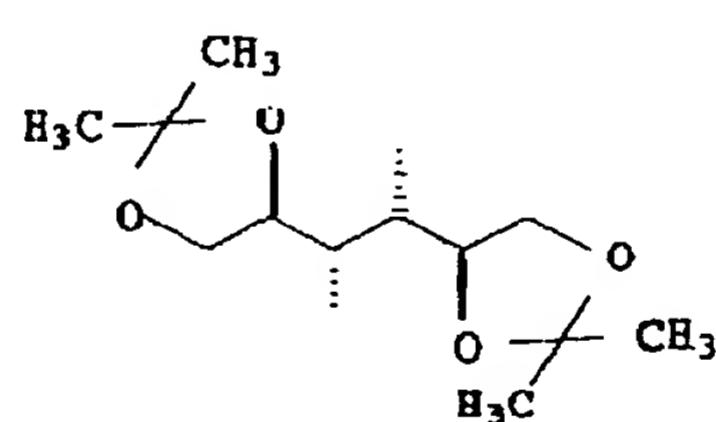
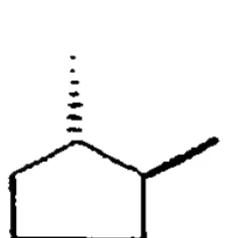
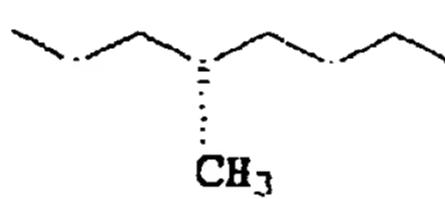
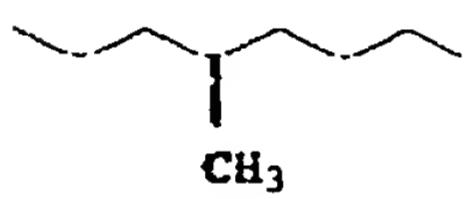
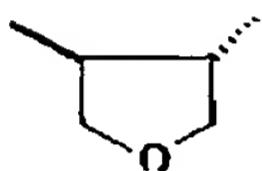
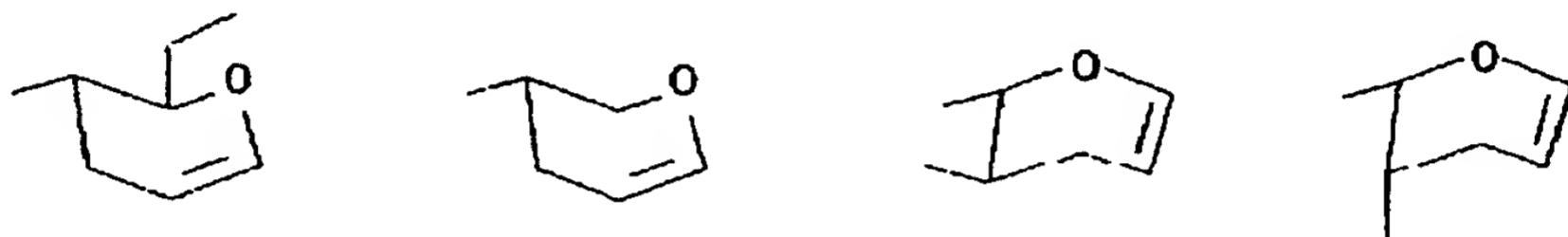
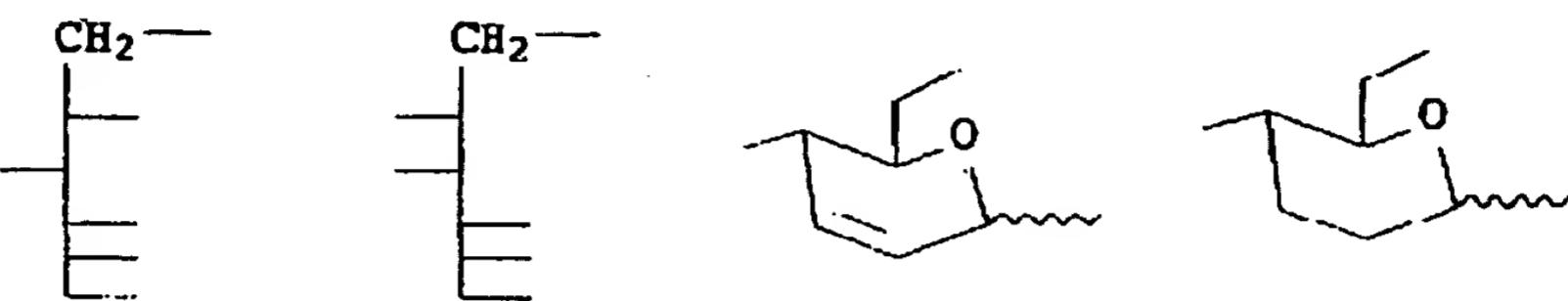
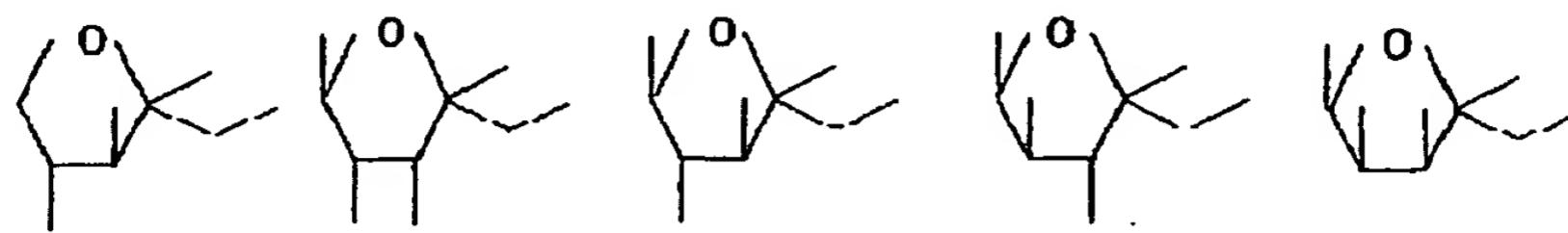
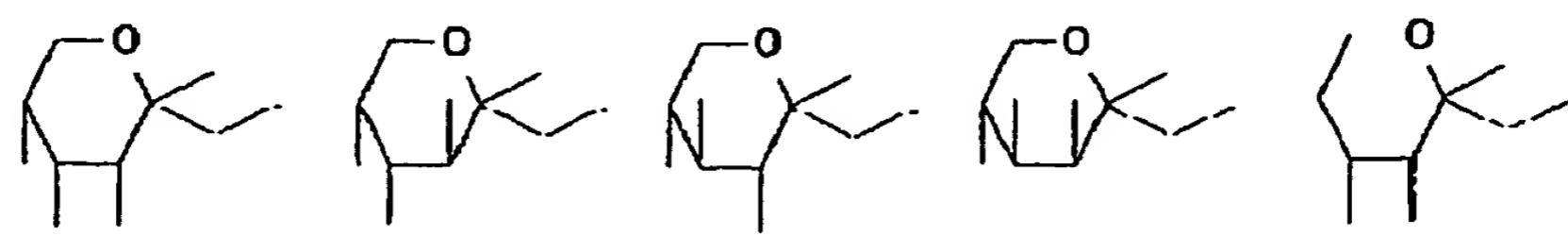
W has the above reported meaning; and

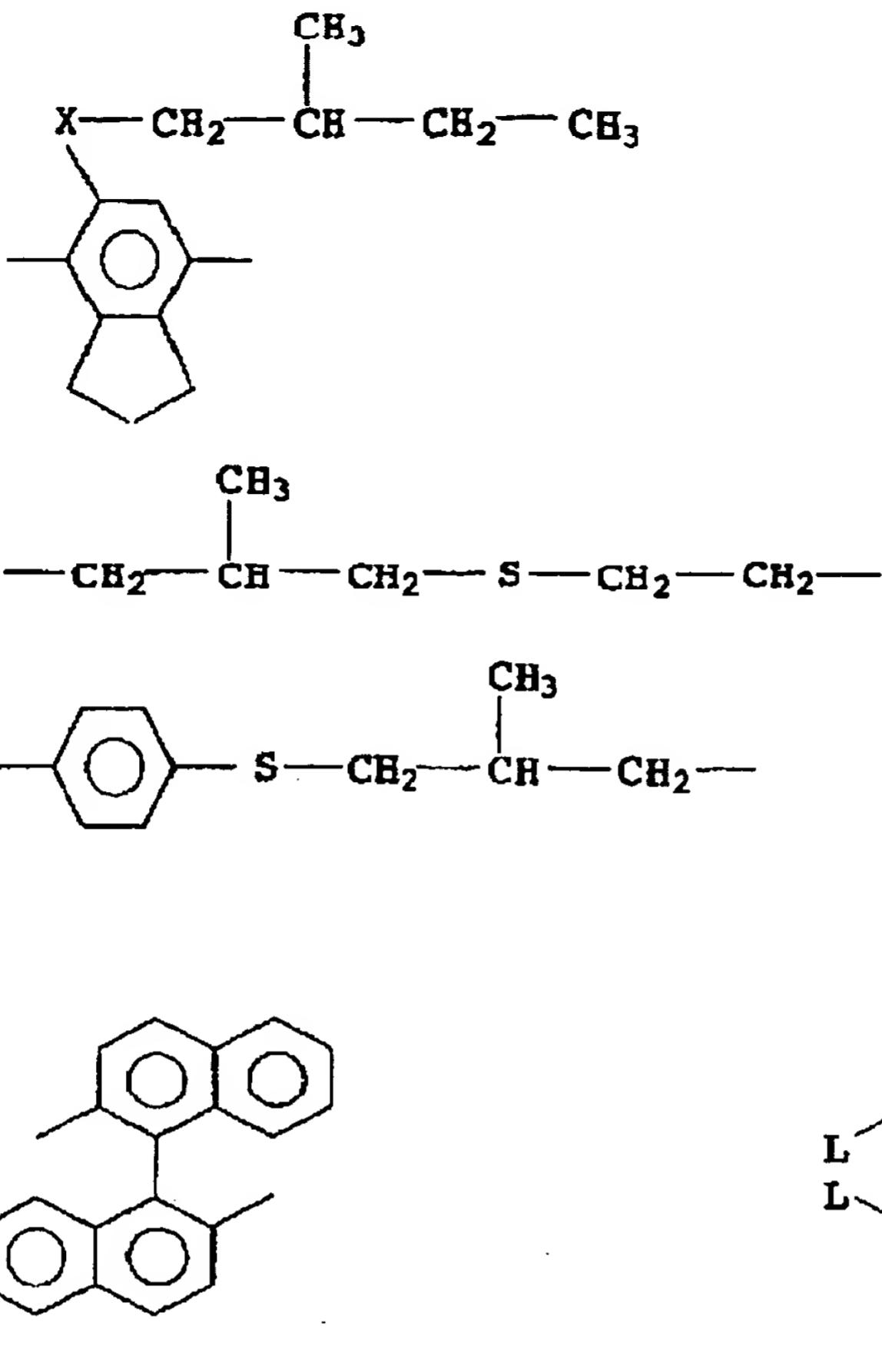
Q preferably stands for a chemical bond or an arylene radical, especially a phenylene or naphthalene radical, possibly substituted with one or more groups selected from C<sub>1</sub>-C<sub>4</sub> alkoxy, fluorine, chlorine, bromine, cyano, hydroxy or nitro.

5. Cholesteric oligomers as in any of the foregoing claims in which the groups A independently of one another are selected from groups of the formulas









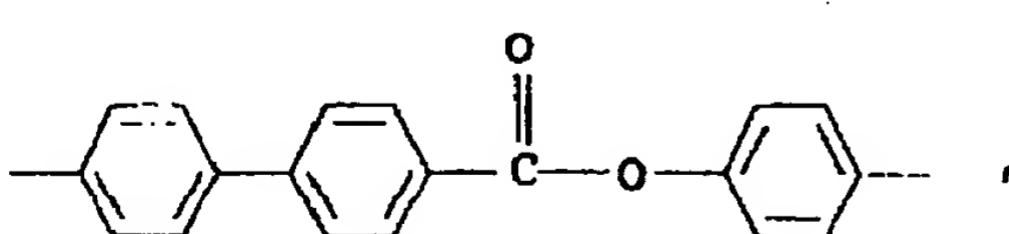
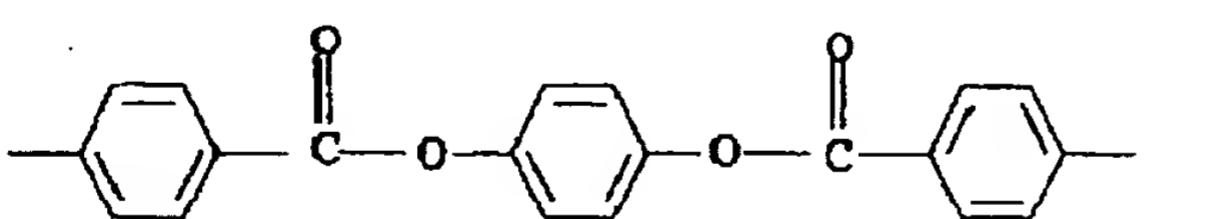
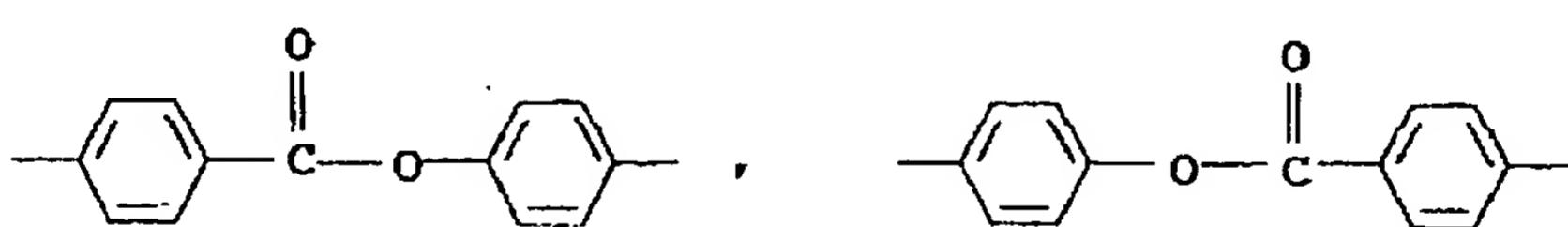
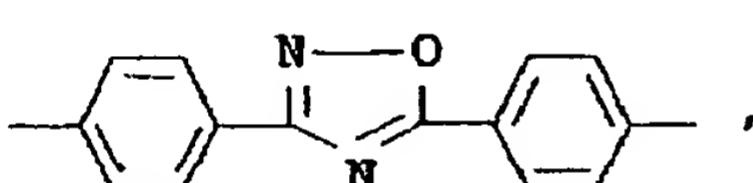
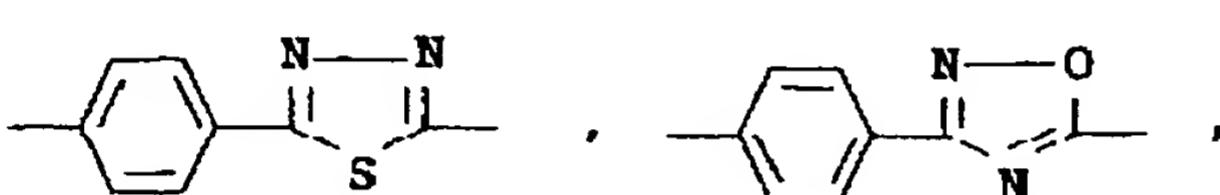
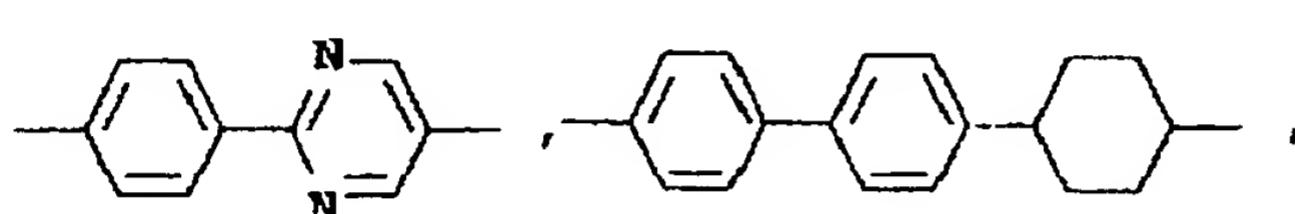
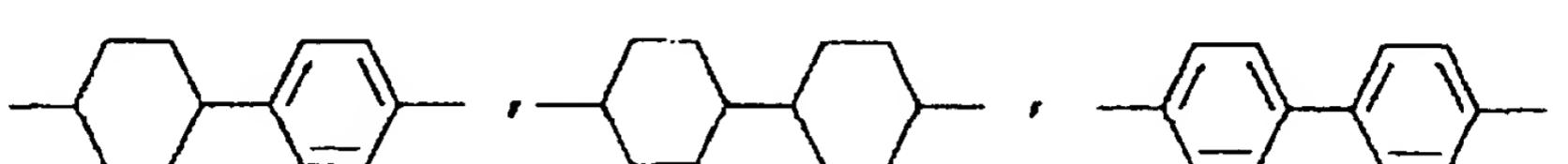
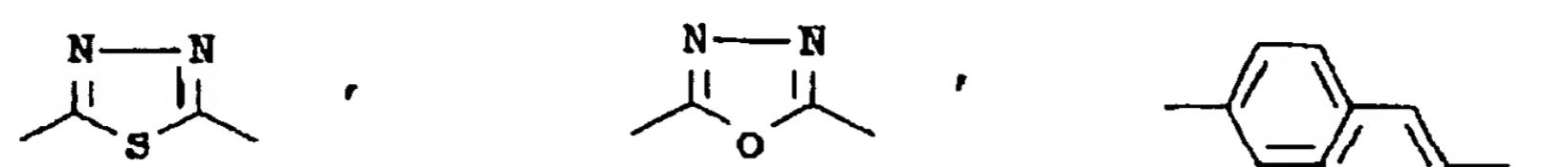
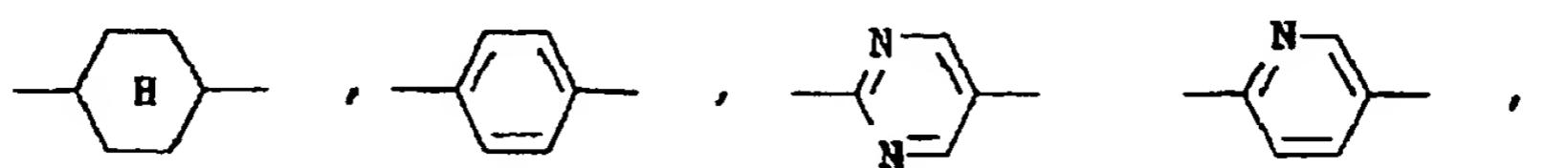
where, in the above formulas:

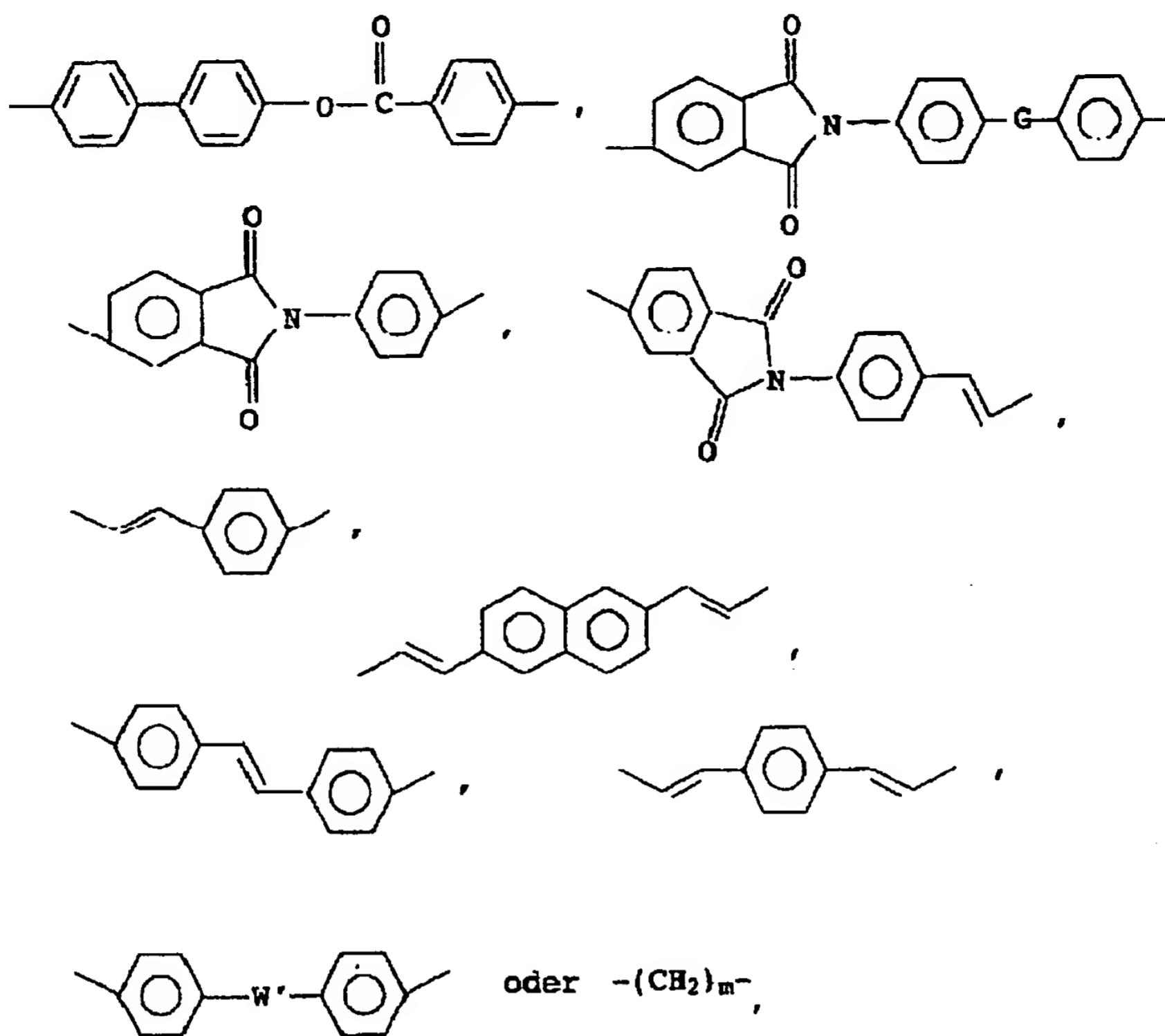
L stands for H, alkyl, alkoxy, alkylthio, halogen, COOR, OCOR, CONHR or NHCOR,

R stands for C<sub>1</sub>-C<sub>4</sub> alkyl or hydrogen, and

X stands for S, O, N, CH<sub>2</sub> or a single bond.

6. Cholesteric oligomers as in one of the foregoing claims in which the groups B independently of each other are selected from the groups of the formulas:





where each of the phenylene groups or naphthyl groups may display 1, 2 or 3 substituents which independently of one another are selected from among the straight-chained or branched C<sub>1</sub>-C<sub>4</sub> alkyls, C<sub>1</sub>-C<sub>4</sub> alkoxy, fluorine, chlorine, bromine, cyano, hydroxy or nitro, where in the above formulas

W' stands for NR, S, O, (CH<sub>2</sub>)<sub>g</sub>O(CH<sub>2</sub>)<sub>h</sub>, (CH<sub>2</sub>)<sub>m</sub> or O-(CH<sub>2</sub>)<sub>m</sub>-O,

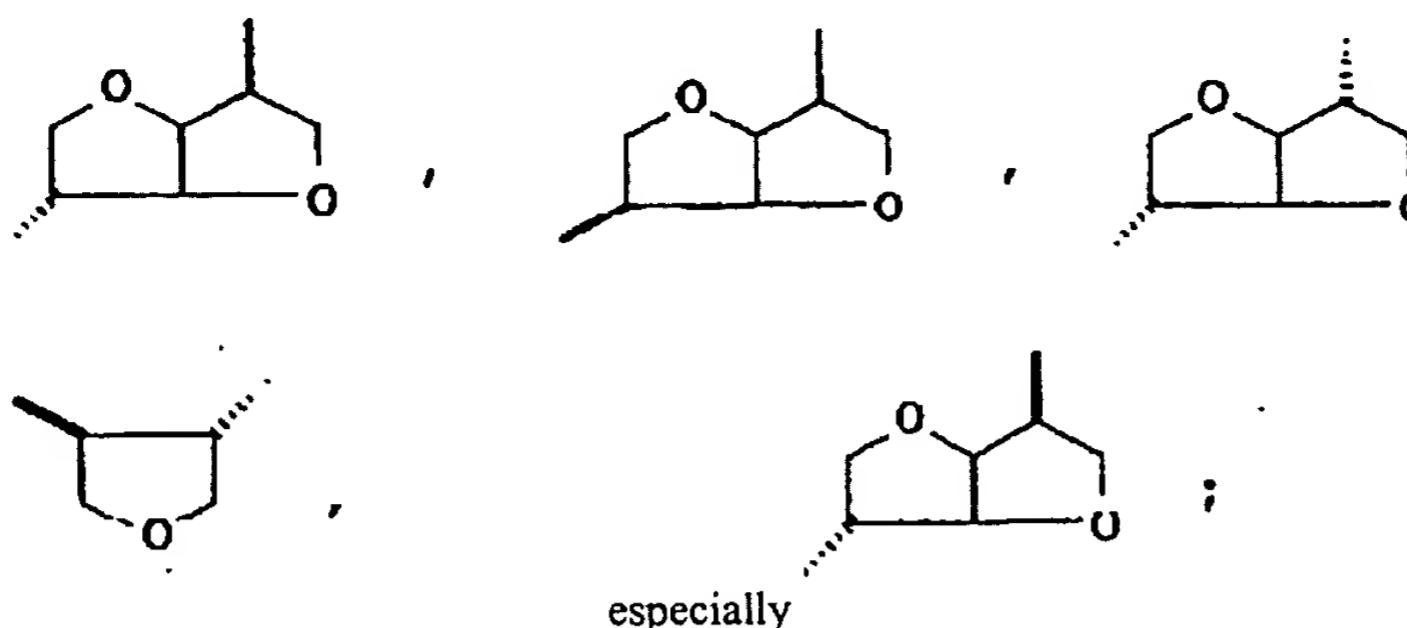
G stands for a single bond, O or S,

R denotes alkyl or hydrogen,

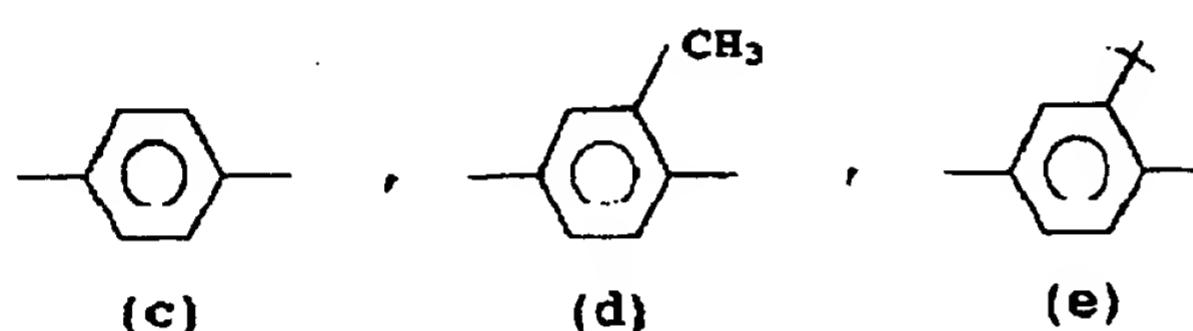
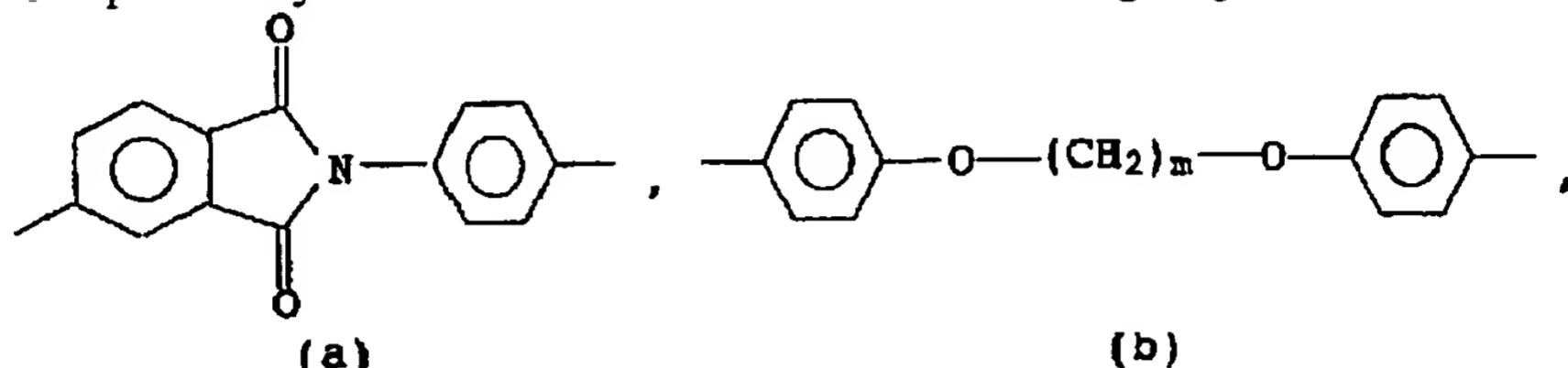
m is a whole number from 1 to 15, and

g and h independently of each other stand for whole numbers from 0 to 10.

7. Cholesteric oligomers as in any of the foregoing claims in which the groups A independently of each other are selected from among groups of the formulas:



the groups B independently of one another are selected from the groups of the formulas:



and  $-(\text{CH}_2)_m-$  especially (a), (d), and/or (e) where  
(f)

(1) where  $m$  stands for a whole number from 4 to 12,

m stands for a whole number from 4 to 10.

the groups Y independently of one another stand for -CO-O- or -O-CO- and

Z stands for

8. Cholesteric oligomers as in any of the foregoing claims in which

q stands for 0.1 to 1,

p stands for 2, and

n stands for 1.

9. Cholesteric oligomers as in any of the foregoing claims which contain the groups A and B and Z in a molar ratio of A/B/Z of about 0.05 to 2/approximately 1 to 30/approximately 0.5 to 5, especially from about 0.1 to 1/about 0.5 to 20/about 1.5 to 2.5 condensed in.
10. Cholesteric oligomers as in one of the foregoing claims whose intrinsic viscosity is about 0.1-3 dl/g, especially 0.1-1.5 dl/g, especially preferably about 0.1 to 0.5 dl/g, measured at 20 C.
11. Cholesteric oligomers as in one of the foregoing claims whose glass transition point lies in the range of about 80-300 C, especially 90-200 C, especially preferably about 90-140 C.
12. Cholesteric polymeric network obtained by heating the cholesteric oligomers as in one of the foregoing claims.
13. Cholesteric polymeric network as in claim 17 obtained by heating at a temperature of about 200-350 C, especially 250-300 C.
14. Process for production of cholesteric oligoesters as in one of claims 1-11 characterized by the fact that free diols of formula A-(OH)<sub>2</sub> are reacted with activated dicarboxylic acids, especially with dicarboxylic acid dichlorides of the formula B-(COCl)<sub>2</sub> and groups or radicals of the formula Z-(OH) and possibly with free diols of the formula B-(OH)<sub>2</sub> in an inert solvent, especially in an inert aromatic solvent, especially preferably 1-chloronaphthalene.
15. Process for production of cholesteric oligocarbonates as in one of claims 1-11 characterized by the fact that free diols of formulas A-(OH)<sub>2</sub> and B-(OH)<sub>2</sub> as well as groups or radicals of the formula Z-(OH) are condensed with phosgene or especially diphosgene.
16. Application of the cholesteric oligomers as in one of claims 1-11 as surface coating materials or for the production pigments.
17. Single-layer or multilayer pigments containing cholesteric oligomers as in one of claims 1-11 or cholesteric polymer networks as in claims 12 or 13.

18. Application of cholesteric polymeric networks as in claims 12 or 13 or pigments according to claim 17 in the vehicle and vehicle accessory sector, in EDP, in leisure time and athletic and game sector, as optical structural components, such as polarizers or filters, in the cosmetic sector, in the textile, leather or jewelry sector, in the gift sector, in writing utensils or on eyeglass frames, in the construction sector, in the domestic sector and in printing products of all types and for the production of paints and enamels, for counterfeiting impeding treatment of articles and for coating of articles of everyday use or for enameling vehicles.

19. Compositions containing at least one pigment as in claims 17.